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U. S. DEPARTMENT OF AGRICULTURE,
BUREAU OF SOILS—BULLETIN No. 30.
MILTON WHITNEY, Chief.

THE MINERAL CONSTITUENTS OF THE SOIL SOLUTION.

BY

FRANK K. CAMERON AND JAMES M. BELL.

WASHINGTON:
GOVERNMENT PRINTING OFFICE.
1905.

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LETTER OF TRANSMITTAL.

U. S. Department of Agriculture,
Bureau of Soils,
Washington, D. C., October 24, 1905.

Sir: I respectfully transmit herewith the manuscript of a technical paper entitled "The Mineral Constituents of the Soil Solution," which I recommend be published as Bulletin No. 30 of the Bureau of Soils.

Respectfully,

Milton Whitney,
Chief of Bureau.

Hon. James Wilson,
Secretary of Agriculture.

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THE MINERAL CONSTITUENTS OF THE SOIL SOLUTION.

INTRODUCTION.

For some years past the Bureau of Soils of the Department of Agriculture has been studying the relation of the chemical properties of the soil to crop production. This study has led to the conclusion, since obviously the growing plant obtains its mineral nutrients directly from the aqueous solution formed by the soil moisture, that the properties of and the phenomena presented by the soil solution must be the first subjects of consideration.

From the data now available it appears that practically all soils contain some of each one of the common rock-forming minerals. It follows that, if equilibrium conditions obtained and no disturbing factors entered, all soils would possess in their soil moisture a nutrient solution of a constant composition. Disturbing factors do enter, however, to some extent, and it is very doubtful if conditions of equilibrium between the soil components are ever completely realized in nature; yet it appears that the generalization stated is more or less closely approximated for some of the important mineral constituents of plant nutrients. It further appears that the minerals continue to dissolve with fresh addition of water, or as the dissolved constituents are removed, and a supply of the necessary plant nutrients is thus kept up indefinitely. The base-carrying minerals are generally true salts, and moreover are not only dissolved by water, but are decomposed through hydrolysis. On the other hand, some synthetic processes may be involved, and it is necessary to consider these facts in order to obtain a clear insight into the relation of the various soil components to one another and to the production of a nutrient medium suitable for plant growth. On account of the relatively large amount of solid surface in contact with the soil solution special chemical considerations are involved. Absorption, adsorption, catalysis, and possibly other surface effects enter, which much modify the chemical phenomena to be expected from a consideration of the same solution under the ordinary conditions realized in a containing vessel.

Of no less importance are the organic constituents of the soil solution, but these will not be considered in the present bulletin, except incidentally as they affect the mineral constituents.

A large mass of data bearing more or less directly upon the points just cited has from time to time been gathered from the literature. In order to establish the views and premises that are fundamental for certain researches which the Bureau has been and is now conducting, it has been deemed advisable to bring together the more important data which the publications of other investigators furnish, together with some further experimental results obtained in the laboratories of the Bureau. The literature bearing on this subject is now very voluminous, confusing, and contradictory. It has not been deemed advisable to undertake a complete bibliography, but it is believed that sufficiently numerous citations have been made to give an accurate idea of the present status of the subject, as well as to demonstrate the points which it is sought to establish in the text.

THE SOIL.

The soil is a heterogeneous mixture containing living organisms and nonliving components, the latter appearing as solids, gases, and a liquid. There is present mineral débris from rock degradation and decomposition; organic matter, the more or less decomposed remnants of former plant and animal tissues; the soil atmosphere, always richer in carbon dioxide and water vapor and possibly other gases than the atmosphere above the soil; living organisms, such as various kinds of bacteria, and often molds, ferments, and enzymes; and finally the soil moisture, a solution of products yielded by the above components and in equilibrium or approaching equilibrium with the solids and gases with which it is in contact.

In its relation to plant life that part of the soil which is of immediate importance is the soil moisture, for it is from this solution that the plants, through their roots, draw all the material involved in their growth, excepting the water and carbon dioxide absorbed through their leaves.[a] Plants can, and it is undoubtedly true that they do, sometimes absorb dissolved organic substances from the soil solution, but such absorptions are probably always adventitious and merely incidental to the growth of the plant in any particular environment. The soil solution is physiologically of the greatest importance, as it is the source from which plants absorb the mineral constituents which have been demonstrated to be absolutely essential to their continued existence and development. The study of the soil solution therefore becomes of the first importance in the investigations of the relation of the soil to plant growth. A number of papers treating various aspects

[a] See Pfeffer, Physiology of Plants, vol. 1, p. 163 et seq., 1900, translated by A. J. Ewart.

of this study have already appeared from this Bureau. In Bulletin No. 17, the general nature of the phenomena involved in the formation of the soil solution has already been discussed. In the following pages there will be given a more detailed discussion of the phenomena involved in the action of ground waters upon the mineral components of the soil.

THE MINERALS IN THE SOIL.

In the degradation and breaking down of the rocks to form soils there result, from the mechanical processes involved, numerous small splinters or fragments of the minerals.[a] To a greater or less extent fragments of these minerals persist in the soil. On the other hand, through the weathering processes taking place in the soil these mineral fragments are more or less decomposed or metamorphosed. There is in the soil an accumulation of silica, generally as quartz grains, an accumulation of hydrated ferric oxide, and perhaps other decomposition products of the original minerals which may more or less mask them, but the original minerals from the rocks can and always do persist in soils derived from those rocks. A number of investigations have been made to determine the minerals in soils,[b] and it would seem from this work that practically all the common rock-forming minerals are to be found in any ordinary arable soil, but that the relative amounts may vary quite widely from those in the rocks from which the soil was formed. This is true even of such substances as potter's or brick clays,[c] the very interesting and thorough work of Ries[d] on the Maryland clays being especially valuable and pertinent in this connection.

Recently Delage and Lagatu[e] have carried out quite thoroughly some very interesting studies on this subject, with the purpose of showing that a mineralogical examination of the soils should be made at least to supplement the usual chemical and mechanical examination. By making a petrographic examination of thin sections made

[a] See Merrill, Rocks, Rock Weathering, and Soils, 1897; Van Hise, U. S. Geol. Survey, Monograph XLVII, A Treatise on Metamorphism, 1904; Shaler, U. S. Geol. Survey, Twelfth Annual Report, The Origin and Nature of Soils, 1890–91, p. 219 et seq.

[b] See, for instance, Chamberlin and Salisbury, U. S. Geol. Survey, Sixth Annual Report, The Driftless Area of the Upper Mississippi, 1884–85, p. 244; F. Steinriede, Anleitung zur Mineralogischen Bodenanalyse, Inaugural Dissertation, Halle, 1889; Dumont, Compt. rend., **140**, 1111 (1905); Merrill, Rocks, Rock Weathering, and Soils, pp. 329 and 358.

[c] Johnstone and Blake, Am. Jour. Sci. (2), **43**, 351 (1867); Cook, Report on New Jersey Clays, 1878, p. 287; Tebier, Compt. rend., **108**, 1071 (1889); Brackett and Williams, Am. Jour. Sci. (3), **42**, 11 (1891); Keyes, Missouri Geol. Survey, Vol. XI, 1896, pp. 49, 95; et al.

[d] Maryland Geol. Survey, Vol. IV., 1902, p. 215 et seq.

[e] Annales de l'école nationale d'agriculture de Montpellier, **4**, 200–220 (1905); Compt. rend., **139**, 1044 (1904).

from the finer soil particles these investigators have found practically all the minerals originally present in the rocks unaltered in the soil. They say:

La terre arable qui, dans tous les traites classiques, est présentée comme le résultat d'une désagrégation et d'une décomposition des minéraux essentiels des roches, nous est apparue, d'une mamière constante, comme un simple produit de désagrégation. Les minéraux y sont à l'état où on les rencontre dans les roches d'origine, c'est-à-dire à un état de pureté, parfaits ou présentant, sans accentuation, les épigénies connues dans les roches. Les feldspaths sont normaux, le quartz normal; de même les micas, la calcite, la tourmaline, l'apatite, le zircon, etc. Ils n'ont subi ni décomposition, ni corrosion localisée.

So important is the work of these investigators that it seems desirable to quote here some of the results attained by them.[a]

Soil from Canton Vaud, Switzerland.—Carbonate of lime abundant in the form of limestone and detrital calcite; hyaline quartz abundant; fragments of schist, chalcedonic quartz, muscovite, biotite, sericite, feldspars, orthoclase, and oligoclase abundant; pyroxene augite, asbestiform amphibole, sphene, zircon, apatite, chlorite, serpentine, ferruginous products (limonite and hematite).

2. *Soil from Tarn, Commune of Parizot.*—Hyaline quartz abundant in large and small fragments; biotite, muscovite, sericite abundant; feldspars, orthoclase and oligoclase; zircon quite abundant; turmaline, asbestiform amphibole, amphibole actinolite, apatite, andaluzite, ferruginous products (hematite, limonite, titaniferous iron), small quantity of fragments of calcite.

3. *Soil from l'Hérault, Commune of Marsillargues.*—Carbonate of lime very abundant in the form of limestone and detrital calcite; granular hyaline quartz very abundant; fragments of quartzite, fragments of silky schist, globular chalcedonic quartz with black cross, feldspars, orthoclase and oligoclase, biotite, muscovite, sericite, tourmaline, sphene, zircon, apatite, ferruginous products (especially limonite).

4. *Soil from l'Aveyron, Commune of Nauviale.*—Carbonate of lime in the form of limestone and detrital calcite, small fragments of dolomite, granular quartz abundant, fragments of quartzite, chalcedonic quartz, fragments of silky schist, fragments of granulite, sericite abundant, biotite, muscovite in small spangles; feldspars, orthoclase, oligoclase, and microcline; apatite, sphene, tourmaline, asbestiform amphibole, ferruginuos products abundant (hematite and limonite).

Cayeux[b] has objected to the statement of Delage and Lagatu, assuming that they did not admit the presence in the soil of the results of metamorphosis and epigenesis, but the latter authors have replied[c] that they recognized and found in soils the results of metamorphic changes, and reiterate that nevertheless the minerals composing rocks were also found as such in the soil resulting from the decomposition of the rocks. Cayeux practically admits the presence in the soil of all the essential minerals of rocks, and adds that the important potash-bearing mineral, glauconite, is present in many of them, but insists that they are all in a more or less decomposed condition.

With the assistance of Dr. Jay A. Bonsteel, of this Bureau, an

[a] Compt. rend., **139**, 1233 (1904).
[b] Ibid., **140**, 1270 (1905).
[c] Ibid., **140**, 1555 (1905).

examination was made of the silt and sand separations from a large number of soils of the United States, including most of the principal agricultural types so far encountered in the surveys by this Bureau. It was found that practically all the common rock-forming minerals could be identified in every soil. It was shown by this examination that, as a general rule, the finer the particles in the separation the less the proportion of quartz and silica, and consequently, one would expect, a higher percentage of the other constituents.[a] It was also conclusively shown by this examination that always, as claimed by Delage and Lagatu, at least some of the mineral species presented clear, unaltered faces, although frequently, especially with the feldspars, alteration products were observed on the mineral fragments.

It should further be considered in this connection that the mineral débris forming the soil has in this very process of formation become much mixed, often, if not generally, the débris from one class or series of rocks being interspersed with the débris of other classes. This mixing process has been so well described in a recent publication by Smith and McCalley[b] that a quotation from their work will be given. They say:

> Since the soils have been derived from the disintegration and decay of the older rocks, a geological map might, to a certain extent, serve also as a soil map, but these products of decomposition now rarely rest upon the parent rock, but have been removed more or less remotely from their place of origin, and after various admixtures have been redeposited upon foreign terranes with which they have no connection. Again, many of the parent rocks of now existing soils have themselves in their turn been soils derived from still older rocks, have been deposited as sediments, compacted, elevated, and again disintegrated and decomposed into soils. These are some of the difficulties which we meet with when we attempt to trace a soil back to its origin.
>
> Another difficulty comes from the fact that soils from various sources have often very similar composition, for all soils are essentially the insoluble residues left from the weathering of older rocks, and these insoluble residues, from whatever parent rock derived, are mixtures in varying proportions of sand and clay, with small amounts of the soluble salts derived from these rocks and not yet completely leached out of the resulting soils. It follows, therefore, that soils from whatever source derived, will differ from each other mainly in the relative proportions of the sandy or siliceous and the clayey constituents.

It thus appears that, speaking generally, all soils contain all the common rock-forming minerals, a generalization announced in a former publication from this laboratory.[c] These minerals are all soluble to some extent in water, although the rate of solution may be quite slow and the actual amount dissolved at any one time may be quite small in comparison with the usual standards.

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[a] See, however, Loughridge, Am. Jour. Sci., 7, 17 (1874); Rep. Agr. Expt. Stat. Univ. California, p. 70 (1892–1894), and Tolman, Rep. Agr. Expt. Stat. Univ. California, Part I, p. 33 (1898–1901).

[b] Geol. Survey of Alabama, The Mineral Resources of Alabama, by Eugene A. Smith and Henry McCalley, 1904, p. 74. See also Merrill, Rocks, Rock Weathering, and Soils, p. 318.

[c] Bul. No. 22, Bureau of Soils, U. S. Dept. Agr., p. 12 (1903).

THE SOLUBILITY OF MINERALS.

That the rock-forming minerals, notably the silicates and alumino or ferro silicates, and similar substances, such as glasses, porcelains, etc., have decided and even measurable solubilities has long been known. Spring waters, well waters, rivers, etc., almost invariably carry considerable quantities of dissolved mineral matter. It has been reported by Ellms and Beneker [a] that the water of the Mississippi in flood time gives an alkaline reaction with phenolphthalein, and the same phenomenon has been often observed with the water of the Potomac as it comes from the laboratory faucet. The water of the Potomac, even when the river is clearest, invariably shows an alkaline reaction after heating in a platinum dish. It seems worth while to call attention briefly to some of the work which has been done along this line of investigation without, however, attempting an exhaustive résumé of the considerable literature bearing upon it.[b]

Wöhler [c] in a classical experiment found apophyllite sufficiently soluble to recrystallize it from water. W. B. and R. E. Rogers [d] found that the following substances when powdered were sufficiently soluble in water to permit a ready examination and sometimes a quantitative analysis of the resulting solution.

Soda feldspar.	Kockolite.	Mesotype.	Lava.
Potash feldspar.	Hypersthene.	Scholezite.	Greenstone.
Lithia feldspar.	Hornblende.	Axinite.	Gneiss.
Glassy feldspar.	Grammatite.	Prehnite.	Hornblende slate.
Labradorite.	Asbestos.	Talc.	Various glasses.
Mica.	Olivine.	Steatite.	Porcelain.
Leucite.	Chalcedony.	Chlorite.	Wedgwood ware.
Tourmaline.	Epidote.	Serpentine.	
Augite.	Analcite.	Obsidian.	

These authors found that from a number of the minerals mentioned above they could obtain from 0.4 to 1 per cent of the mineral in solution by digesting for forty-eight hours. Most of the minerals, when powdered in an agate mortar and treated with pure water, gave an alkaline reaction to litmus. They found that the magnesia-bearing minerals or those in which the magnesium was partly replaced by ferrous iron were the more readily affected, an observation which appears to be confirmed by work done in this laboratory.

Dölter [e] studied the action of water on pyrites, galena, zincblende, stibnite, arsenopyrites, bournonite, copper pyrites, tinstone, rutile,

[a] Jour. Am. Chem. Soc., **23**, 429 (1901).

[b] For an interesting discussion of the older literature, the reader is referred to Bischof's Chemical and Physical Geology, vol. 1, p. 52 et seq., 1854.

[c] Jahresb. Liebig und Kopp, 1847–48, p. 1262.

[d] Am. Jour. Sci. and Arts (2), **5**, 401 (1848).

[e] Monatsh., **11**, 151 (1890).

hematite, heulandite, anorthite, natrolite, and chabazite. He found all these minerals more or less soluble in water. Working in a sealed tube at 80° C. he found that pyrites gave a solution with an acid reaction. He obtained an alkaline reaction with other sulphides and the oxides, but this may have been due to the solubility of the glass tubes.

Johnstone's studies on the action of water on olivine,[a] on the micas[b] and on minerals and rocks,[c] Spezia's work on apophyllite,[d] Skey's[e] work on the detection of the alkalinity of minerals and salts by test papers, Dietrich's[f] and Beyer's[g] work on the effect of water and salt solutions on rocks and soils, Ebelmen's[h] early studies on rock decomposition, Sestini's[i] very interesting study of the action of water on natural metasilicates in mass and in the soil, Gonnard's[j] work on the production of zeolites in the cold, the classical investigations of Daubrée,[k] the observations of Pemberton,[l] Haushofer,[m] Cossa, Müller,[n] Stoklasa,[o] Lemberg,[p] Clar,[q] and many others show that from an early date to the present time it has been recognized that the rock-forming minerals are measurably soluble in water. Recently Clarke[r] has found that muscovite, lepidolite, phlogopite, orthoclase, oligoclase, albite, leucite, nephilite, cancrinite, sodalite, spodumene, scapolite, laumontite, stilbite, chabazite, heulandite, thomsonite, analcite, natrolite, pectolite, and apophyllite all dissolve in water, giving an alkaline reaction to the solution, as shown by the addition of alcoholic phenolphthalein. The magnesium-bearing micas are more soluble than muscovite, albite more than orthoclase, with oligoclase between, an observation in harmony with Lemberg's[s] experiments, and the general experience of geologists.[t] Several rock powders were tested by treating with water and phenolphthalein, a granite, and an amphibole gabbro, not showing any alkaline reaction.

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a Proc. Roy. Soc. Edinburgh, **15**, 438 (1887–88); **16**, 172 (1888–89).
b Quar. Jour. Geol. Soc., **45**, 363 (1889).
c Trans. Edinburgh Geol. Soc., **5**, (II) 282 (1887).
d Jahrb. f. Min., 1895, II, Rep. 242.
e Chem. News, **27**, 221 (1873).
f Landw. Vers.-Stat., **14**, 314 (1871).
g Jahresb. Agr. Chem., Hoffman, 1862–63, p. 12.
h Ann. des Mines (4), **7**, 3 (1845); (4) **12**, 627 (1847).
i Atti. Soc. Tosc. di Sc. Nat., Pisa, Proc. Verb., **12**, 127 (1900).
j Jahrb. f. Min., 1884, I, Ref. 28.
k Compt. rend., **44**, 997 (1857); Géologie Expérimentale, 1879, p. 268 et seq.
l Chem. News, **47**, 5 (1883).
m Jour. prakt. Chem., **103**, 121 (1868).
n Tschermak's Min. Mitth., 1887, p. 25.
o Landw. Vers.-Stat., **27**, 197 (1882).
p Zeit. deutsch. geol. Ges., **35**, 575 (1883).
q Jahrb. f. Min., 1884, p. 229.
r Jour. Am. Chem. Soc., **20**, 739 (1898); Bul. No. 167, U. S. Geol. Survey, p. 156 (1900).
s Zeit. deutsch geol. Ges., **35**, 575 (1883).
t Merrill, Rocks, Rock Weathering and Soils, p. 234 et seq.

But an alkaline reaction was obtained with rhyolite, trachite, leucite basalt, feldspar basalt, diorite, granite, gneiss, phonolite, diabase, and camptonite. On standing, the color produced by adding phenolphthalein to the solutions in contact with the minerals gradually faded out of the supernatant solution, which Clarke attributed to a probable action of light. But with some of the minerals the disappearance of the color was relatively quite rapid, the coloring matter being collected on the settled powder at the bottom of the vessel. Van Hise[a] apparently thinks that there is a real distinction thus shown, the minerals falling into two classes, but work in this laboratory has shown conclusively that the true explanation is that the coloring matter is absorbed on the surface of the very finely divided suspended particles and is carried down with them. Steiger[b] has followed up this work of Clarke by making quantitative measurements of the solution products of many of the minerals.

Finally, Cushman[c] has tested the action of water upon the powders of a large number of rocks, including the following:

Quartzite.	Epidosite.	Altered diabase.	Syenite.
Banded chert.	Altered peridotite.	Slate.	Basalt.
Dolomite.	Chert.	Eclogite.	Argillite.
Granite.	Sandstone.	Quartzite breccia.	Arkose.
Gneiss.	Limestone.	Feldspathic sandstone.	
Diabase.	Hornblende granite.	Dolomitic limestone.	
Feldspathic basalt.	Arkosic gneiss.	Gneissoid granite.	

All these rock powders yielded solutions which showed an alkaline reaction with phenolphthalein, excepting the cherts, quartzites, and some specimens of sandstone, granite, slate, and syenite. Other specimens of sandstone, granite, slate, and syenite, however, did yield solutions which showed an alkaline reaction.

Enough data has been cited to show that rocks and the minerals of which they are composed are soluble in water, and that where minerals containing the alkalies or alkaline earths are combined with silicic, alumino-silicic or ferro-silicic acids, the solution formed has an alkaline reaction.

Soil extracts, although containing dissolved mineral matter in measurable quantities, the bases predominating over the mineral acids are usually either neutral or faintly acid to litmus. On boiling in platinum vessels, however, to eliminate carbon dioxide or possibly other volatile acids, in the vast majority of cases the solution will show an alkaline reaction with iodoeosine, phenolphthalein, or litmus. Aqueous extracts were prepared from a number of soils and freed of all suspended matter by filtering under pressure[d] through

[a] A Treatise on Metamorphism, U. S. Geol. Survey, Monograph XLVII, p. 86 (1904).

[b] Bul. No. 167, U. S. Geol. Survey, p. 159 (1900).

[c] Bul. No. 92, Bureau of Chemistry, U. S. Dept. Agr., 1905, pp. 6–7.

[d] See Briggs, Bul. No. 19, Bureau of Soils, U. S. Dept. Agr., 1902.

Pasteur-Chamberland filter tubes. An alkaline reaction was shown by extracts thus prepared from the following soils taken at random from the collection of the Bureau:

Cecil clay, N. C.
Podunk fine sandy loam, Conn.
Sea Island Cotton, S. C.
Sharkey clay, La.
Penn loam, Md.
Loess, Ill.
Trenton limestone, Md.
Hagerstown loam, Md.
Hagerstown clay, Md.
Plains marl, Nebr.
Gabbro, Md.
Norfolk sand, Md.
Elkton loam, N. J.
Leonardtown loam, Md.
Sassafras sandy loam, Md.
Heavy black adobe, Cal.
Clarksville clay loam, Tenn.
Porters black loam, N. C.
Sandhill, S. C.
Miami silt loam, Ill.
Susquehanna loam, Md.
Marion silt loam, Ill.

Samples of the following soils, however, did not give extracts which were alkaline after boiling:

Susquehanna clay.
Brightwood clay.
Cecil sandy loam.
Marion silt loam (subsoil).
Memphis silt loam.
Leonardtown loam (subsoil).
Conowingo barrens.
Portsmouth sandy soil.
Cecil loam (subsoil).

It thus appears that in the soil the minerals behave toward water in the same way as do the same minerals when isolated or when mixed in a rock powder. The appearance of an alkaline reaction in the solutions which are yielded, denoting an excess of bases over acids among the solutes, is of special significance and warrants further consideration at this point.

THE HYDROLYSIS OF MINERALS.

By far the greater number of soil or rock forming minerals are composed of the strong base-forming metals with silicon and aluminum, or of silicon and ferric iron, or silicon, aluminum, and ferric iron, together with oxygen. Constitutionally they may be regarded from several points of view, each of which is legitimate and has certain advantages.[a] They may be considered as made up of combinations of the oxides. For example, orthoclase may be considered to be represented by the formula $K_2O.Al_2O_3.6SiO_2$. This does not, however, imply any retention of the old "dualistic hypothesis" of Berzelius, which even to the present day has appeared to have a real living value to mineralogists. This point of view is especially advanta-

[a] Of the many treatises referring to this subject now available the reader is referred especially to F. W. Clarke, The Constitution of the Silicates, Bul. No. 125, U. S. Geol. Survey (1895), and J. H. L. Vogt, I. Über die Mineralbildung in Silikat-Schmelzlösungen (1903.) II. Über die Schmelzpunkt-Erniedrigung der Silikatschmelzlösungen. Christiania (1904).

geous in studying melts and rock magmas, as in the recent work by Baur,[a] by Richardson,[b] and by Day and Allen.[c]

Minerals may be considered as "molecular compounds" of two or more silicates analogous to alum, where, although the solid phase is evidently a definite molecular species, yet in aqueous solution, in so far as our present knowledge goes, the solutes appear to be a mixture of potassium sulphate and aluminum sulphate. From this point of view orthoclase would be expected to dissolve with the formation of potassium metasilicate and aluminum silicate. A serious objection to the supposition, however, is that no formula can be written for such a mineral as orthoclase on this basis without assuming the presence of two different acids. One may assume the minerals to be double salts of a complex acid, silicon atoms being united through oxygen atoms. Thus orthoclase would be written $(KO)Si_3O_4(O_3Al)$ as the salt of an acid $H_4Si_3O_8$. The principal argument in favor of this supposition is that it does permit of writing a rational formula on the basis of a tetravalency for silicon.

From another point of view the aluminum or the ferric iron may be considered an essential constituent of the acid radical. Thus orthoclase, $K.AlSi_3O_8$, would be the potassium salt of a hypothetical acid $H.AlSi_3O_8$. This point of view has much to commend it when studying solution phenomena. Aluminum is very weak as a base-forming element, as is also ferric iron, and both in the presence of stronger bases readily act as acid-forming elements. There are, moreover, many analogies now known. For instance, Ostwald[d] and Hittorf have shown that the well-known "double chloride" of potassium and platinum behaves in solution as the potassium salt of a chlor-platinic acid, H_2PtCl_6. This supposition as to the constitution of the silicate minerals makes much more easily understood the formation of an alkaline solution as the result of a simple hydrolysis, and leads to a comparatively simple view of what are usually regarded as the very complex relations between the metamorphic products in the zone of weathering.[e]

It is a recognized fact that in the soil generally in the zone of weathering there is a predominating tendency for the complex silicates to decompose with the separation of silica as quartz or in some other form.[f] It is often supposed that this decomposition is effected

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[a] Zeit. phys. Chem., **42**, 567 (1903).

[b] The Constitution of Portland Cement; address before the Association of Portland Cement Manufacturers at Atlantic City, N. J. (1904).

[c] Am. Jour. Sci., **19**, 93 (1905).

[d] Ostwald, Foundations of Analytical Chemistry, 1895, p. 50. Translated by McGowan.

[e] See Van Hise, loc. cit., pp. 43 and 163.

[f] The separation of silica on decomposition of silicates was early recognized by Fournet [Ann. Chim. Phys., **55**, 225 (1833)], Brongniart [Arch. du Museum, Vol. I (1839)], and others. Ebelmen [Ann. des Mines (4), **7**, 3 (1845)], seems to have been the first to show that it was a general property of the silicate minerals, whether they contained basic constituents or not.

mainly by dissolved carbon dioxide, which is always present in the water in the soil or rock and mineral crevices. This explanation is, however, very doubtful, since carbonic acid, supposing it to exist, can not be much, if any, stronger than the silicic acid, is much more soluble, and is readily volatile. It is much more probable that the silica separates from silicic acids formed by hydrolysis of the corresponding salts, because these acids are unstable under the particular conditions existing in the solution in which they are formed, as, for instance, would be hypochlorous and many other acids when the bases to which they are joined are removed. The carbon dioxide undoubtedly has an indirect effect in increasing the amount of hydrolysis by reducing the active mass of the hydrolized base through the formation of bicarbonates.

The minerals composing rocks and soils are for the most part salts of a strong base or bases, sodium, potassium, calcium, magnesium, ferrous iron, manganese, etc., combined with a weak acid, silicic, aluminic, alumino-silicic, ferro-silicic, etc. Water therefore not only dissolves them, but reacts with them or hydrolizes them, as is evidenced by the alkaline reaction of the solution when a pulverized rock or mineral is shaken up with water free from dissolved carbon dioxide. This process of hydrolysis is a familiar one in the case of sodium carbonate, which is always more or less hydrolized to sodium bicarbonate[a] and sodium hydrate, thus:

$$Na_2CO_3 + HOH \rightleftarrows NaHCO_3 + NaOH,$$

and the resulting solution gives an alkaline reaction on account of the hydrolized sodium hydrate. Calcium carbonate, in the same way, is partially decomposed, and yields calcium hydrate essentially thus:

$$CaCO_3 + H_2O \rightleftarrows Ca(OH)_2 + CO_2 + H_2O.$$

The hydrolysis of calcium carbonate and magnesium carbonate has been studied by Bodländer,[b] who has obtained quantitative figures for these salts. The common Bohemian glasses from which much of our laboratory apparatus is made are sodium calcium alumino-silicates, and are so soluble that if water free from carbon dioxide be kept standing in a vessel made from them for some hours the presence of dissolved alkali can be detected by the addition of phenolphthalein or by the decrease in electrical resistance.[c] Such vessels will usually impart an alkaline reaction to the solution within a few minutes if raised to the boiling temperature, and even our

[a] Cameron and Briggs, Bul. No. 18, Bureau of Soils, U. S. Dept. Agr. (1901), p. 9; Jour. Phys. Chem., **5**, 537 (1901); McCoy, Am. Chem. Jour., **29**, 437 (1903).

[b] Zeit. phys. Chem., **35**, 31 (1900).

[c] Whitney and Means, Bul. No. 8, Divisions of Soils, U. S. Dept. Agr., 1897, p. 15.

most resistant glassware is noticeably dissolved and hydrolized at the latter temperature.[a] In fact the solubility of glass is a recognized source of errors in analytical work. It is worthy of note in this connection that hydrolysis is markedly increased by even moderate rise in temperature, a fact of very great significance to geology and soil chemistry.

That orthoclase is dissolved by water and hydrolized is shown by the fact that it yields a solution alkaline to phenolphthalein, litmus, and similar indicators. If we assume, for clearness in writing, ideal formulas, this may be expressed thus:

$$KAlSi_3O_8 + HOH = KOH + HAlSi_3O_8.$$

The potassium hydrate thus formed may unite with carbon dioxide to form carbonates or bicarbonates, or with other acids, forming salts more soluble than the orthoclase or the hydrolized acid, and may thus be removed. But under ordinary conditions the hydrolized acid $HAlSi_3O_8$ seems to be unstable. Silica in the form of quartz or otherwise is split off in greater or less amounts as thus indicated:

$HAlSi_3O_8 - 1SiO_2 = HAlS_2O_6$ . . . Pyrophyllite.
$HAlSi_3O_8 - 2SiO_2 = HAlSiO_4$ . . . Kaolinite or kaolin.
$HAlSi_3O_8 - 3SiO_2 = HAlO_2$ . . . . Diaspore.

All three of these methods of decomposition or "metamorphism" have been observed in nature, the second being the most common and probably the only one of importance under soil conditions.

This method of regarding the process of "kaolinization" or metamorphism of feldspars has distinct advantages. It is undoubtedly a perfectly general process. It does not require the assumption that carbon dioxide has any special function in the process, an assumption which is altogether improbable at ordinary temperatures and pressures. This view can moreover be shown to be in harmony with all the known data concerning such metamorphism; it is strictly analagous to many well known and understood laboratory studies, and it does not necessarily involve any hypotheses, such as electrolytic dissociation, etc., but is based alone on the observed facts that with

[a] Gmelin-Kraut, Anorganische Chemie, vol. 2, 1904; Emmerling, Ann. Chem. Phar., **150**, 257 (1869); Ber., **9**, 1540 (1876); Kreuzler and Henzold, Ber., **17**, 34 (1884); Cowper, Jour. Chem. Soc., **41**, 254 (1882); Bohlig, Zeit. anal. Chem., **23**, 518 (1884); Wartha, Zeit. anal. Chem., **24**, 220 (1885); Egger, Dingl. Poly. Jour., **225**, 127 (1885); Pfeiffer, Ann. Phys. Chem. (2), **44**, 239 (1891); Wied. Ann., **31**, 831 (1887); Schott, Zeit. Instr., **9**, 86 (1889); Barus, Am. Jour. Sci., (3), **41**, 110 (1891); Mylius and Foerster Ber., **22**, 1092 (1889); **25**, 97 (1892); Zeit. Instr., **9**, 117 (1889); **11**, 311 (1891); Mylius, Zeit. Instr., **8**, 266 (1888); **9**, 56 (1889); Foerster, Ber., **25**, 2494 (1892); **26**, 2915 (1893); Warburg and Ihmon, Wied. Ann., **27**, 491 (1886); Kohlrausch, Wied. Ann., **44**, 577 (1891); Ber., **24**, 3560 (1891); **26**, 2998 (1893); Liebermann, Ber., **31**, 1818 (1898); Walker, Jour. Am. Chem. Soc., **27**, 865 (1905); et al.

water the feldspars give an alkaline reaction, and that quartz or other forms of silica, together with one or more of the other substances indicated, are formed.

Kahlenberg and Lincoln[a] have shown that probably, in very dilute solutions of the silicates, the hydrolysis is practically complete and the silica is all present as colloidal silica and not as silicic acid. Nevertheless, at higher concentrations silicates are formed, and there is abundant evidence in nature that the alumino or ferro-silicates are constantly uniting with bases to form salts, such, for example, as the micas.[b] In the decomposition of the orthoclase, for instance, some of the potassium hydrate formed may well be expected to react with kaolin to form muscovite in accordance with the following equation:

$$HAlSiO_4 + KOH \rightleftarrows KAlSiO_4.2HAlSiO_4 + HOH.$$

Whether muscovite is to be regarded as a definite compound of the composition indicated, or an isomorphous mixture of an acid and its salt is yet uncertain, but the variation in the composition of the mixed alkali micas and the fact that muscovite and kaolinite are both monoclinic argue for the latter assumption. One may then regard these micas as isomorphous mixtures of salts of kaolinite with the acid itself. In a similar manner in the alteration of albite to pyrophyllite the latter may react with some of the liberated soda to form analcite,

$$HAlSi_2O_6 + NaOH \rightleftarrows NaAlSi_2O_6.H_2O.$$

With a different concentration of alkali, the feldspars may undergo another metamorphosis, yielding zeolites as the alteration of albite to heulandite,

$$NaAlSi_3O_8 + Ca\ (OH)_2 + H_2O = Ca(AlSi_3O_8)_2nH_2O + NaOH.$$

In some cases, however, the formation of a zeolite from a feldspar seems to be the taking up of water alone to form a solid solution with or without change of the crystal system, but always with change of the morphological, optical, and other physical properties.

The amount of water present is given in the above formula in the form indicated as indefinite rather than in one of the forms usually found in the text-books, since Tammann[c] has shown that this, as well as other zeolites, is in fact a solid solution of water in the mineral, and it would seem to be a question worthy of serious consideration whether the term "zeolite," which now possesses but a very

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[a] Jour. Phys. Chem., **2**, 88 (1898).

[b] Van Hise, loc. cit., p. 693.

[c] Wied. Ann., **63**, 16 (1897); Zeit. anorg. Chem., **15**, 318 (1897); See also observations on Wellsite by Pratt and Foote, Am. Jour. Sci. (4), **3**, 443 (1897); Zeit. Kryst. Min., **28**, 581 (1897).

indefinite significance, should not be restricted to such solid solutions of water in alumino-silicates.

These views are much strengthened by the observations of Friedel[a] that the water in zeolites can be replaced by ammonia and other gases, and the further observations of Rinne[b] that dehydrated chabazite can take up carbon disulphide, carbon dioxide, alcohol, chloroform, benzene, or aniline in place of the water removed.

Van Hise[c] states that while the alteration of feldspars and other minerals to zeolites probably does take place to some extent in the belt of weathering (and therefore perhaps in the soil) the tendency is in the other direction, that is, the alteration of the zeolite to feldspar or even further decomposition. The significance of the zeolites from the point of view of the soil investigator has been assumed rather than proved,[d] as has been clearly pointed out by Merrill,[e] and they need not be considered further here.

The hydrolysis of the essentially magnesian minerals is especially interesting for the reason that in common with other salts of magnesium which hydrolize[f] there seems to be a strong tendency to the formation of true basic salts. Thus in the alteration of pyroxene, amphibole, and olivine to chlorite or serpentine, there seems to be a basic salt formed or possibly a solid solution of the hydrate and the silicate. This can be illustrated simply by the following scheme,

$$MgSiO_3 + HOH = MgSiO_3.nMg(OH)_2 + SiO_2,$$

which is analagous to the suggestion of Bodländer[g] regarding the reaction of magnesium carbonate with water,

$$MgCO_3 + HOH = MgCO_3.nMg(OH)_2 + CO_2.$$

Daubrée's[h] experiment where he found that by fusing serpentine, enstatite and olivine were formed, seems to be a reversal of this reaction. Many other examples might be given, and undoubtedly all the common alterations of the silicates produced by water can be shown to be in harmony with the ideas just presented. The examples cited, however, are believed to be sufficient for the purpose of developing the point of view from which the silicates and their reactions with the soil water have been regarded in this investigation. The extent

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[a] Bul. Soc. Min., **19**, 94 (1896).

[b] Jahrb. f. Min., **2**, 28 (1897).

[c] Loc. cit., p. 333.

[d] See Bul. No. 17, Bureau of Soils, U. S. Dept. Agr.

[e] Rocks, Rock Weathering, and Soils, pp. 370 and 374.

[f] Bodländer, Zeit. phys. Chem., **35**, 31 (1900); Cameron and Seidell, Jour. Phys. Chem., **7**, 578 (1903).

[g] Zeit. phys. Chem., **35**, 31 (1900).

[h] Compt. rend., **62**, 661 (1866).

to which the reactions will proceed and the controlling conditions must next be considered.

The minerals or particular molecular species that will remain in contact with or separate from the solution yielded by a mineral or rock powder, or the soil, are conditioned by the concentration of the solution with respect to the constituents of the mineral, the temperature, the pressure, and the presence of other solutes. If we neglect or avoid the presence of other solutes and regard the pressure as practically constant for soil conditions, then, since the solubility of the other constituents are relatively very small, the mineral species are practically determined by the concentration with respect to the base-forming elements and the temperature. In principle the system is similar to many others which have been studied, as, for instance, the system calcium sulphate-potassium sulphate-water,[a] in which at 25° C. gypsum ($CaSO_4 2H_2O$) alone is the only stable solid in contact with solutions containing less than 14.5 grams potassium per liter, while only the double sulphate, syngenite [$K_2Ca(SO_4)_2.H_2O$], can remain in equilibrium with solutions containing amounts of potassium greater than 14.5 grams per liter and less than some yet higher concentration at which potassium sulphate itself separates as a solid phase. The application of the phase-rule principles to the study of such solutions often presents great difficulties on account of the multiplicity of components, the presence generally of disturbing solutes, but more especially even in pure solutions, the fact that the rates of solution and probably also of formation are very slow indeed, and it is practically impossible to obtain and observe the systems under definite conditions at equilibrium. Nevertheless the phase-rule point of view is most suggestive, in that it indicates lines of experiment which, should the time element not prove insurmountable, would make it possible to determine under what conditions the synthetical production of our common rock-forming minerals can be accomplished, working only with aqueous solutions. That this would be possible has already been shown by Lemberg's[b] formation of analcite by treating leucite with a solution of sodium chloride and the reverse reaction with the formation of leucite by treating analcite with a solution of potassium chloride.

The views just developed as to the mechanism of metamorphism in the soil are in full accord with the notable work of Delage and Lagatu,[c] and it seems most probable that the formation of secondary products is in all cases the result of solution and hydrolysis with recombination and crystallization of dissolved materials. In this

[a] Van't Hoff and Wilson: Sitzungsber. Akad. Wiss., Berlin, 1900, p. 1142; Cameron and Breazeale, Jour. Phys. Chem., **8**, 335 (1904).

[b] Zeit. deutsch. geol. Ges., **28**, 537 (1876).

[c] Annales de l'école nationale d'agriculture de Montpellier, **4**, 200–220 (1905); Compt. rend., **139**, 1044, 1233 (1904); **140**, 1555 (1905).

way alone is it rational to expect the continued existence in the soil of the minerals in such a state of purity as they have been shown to possess.

The accumulation of silica in the soil is in full accord with these views. The accumulation of ferruginous products is readily explained. The complete solution and decomposition of ferro-silicates or those in which ferric iron is more or less replacing aluminum would naturally yield the ferric hydrates. But it seems altogether probable that by far the greater part of the ferric hydrate comes from the hydrolized ferrous iron, which, as a base, is found so largely replacing magnesium in the essentially magnesium-bearing minerals. The hydrolized ferrous hydrate would, of course, be promptly oxidized to the ferric condition by the oxygen in the soil atmosphere.

It is noteworthy, however, that alumina, either as gibbsite or bauxite, is but seldom found in soils. In the experience of the writers, covering the examination of several thousand soils from all parts of the United States, aluminum hydrate as such has been observed in but one soil, which came from southern California. Liebrich,[a] in his studies on the formation of bauxite and allied minerals, calls attention to the fact that alumina is not liberated from silicates by ordinary weathering agencies, and it is of much less common occurrence than the iron oxides or hydrates.[b] The mineralogical or petrographical examinations of soils does not generally show the presence of diaspore, gibbsite, or bauxite, although it is quite possible that if they were especially sought examples could be found in which these minerals are components. Our own experiments have failed to show any evidence of the presence of an aluminum hydrate in the solutions formed by the action of water upon the alumino-silicates. It is altogether probable, therefore, that alumina or aluminum hydrate is but very seldom if ever a normal component of soils. From this conclusion it follows necesarily that diaspore or gibbsite is not a normal product of the metamorphism of feldspars under soil conditions; and, further, it indicates that the aluminum is an essential constituent of the acid radical in the alumino-silicates, another justification of the formulas and views advanced above as to the mechanism of metamorphism in the soil through the solution and hydrolysis of the minerals.[c]

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[a] Zeit. prakt. Geol., 1897, p. 212.

[b] See, however, Parmentier, Compt. rend., **132**, 1332 (1901).

[c] It seems probable that the ferric hydrate and aluminum hydrate (if the latter be present) may form ferrates and aluminates, acting thus as carriers of bases. On the other hand, being made more soluble thereby, they are readily transported, and are again precipitated as in the formation of hardpans or conglomerates. Landrin [Compt. rend., **94**, 1054 (1882)] denies the existence of calcium ferrates, and on the whole the formation of iron concretions and hardpans is more readily explained as a result of the action of carbon dioxide. [Bul. No. 17, Division of Soils, U. S. Dept. Agr., 1901, p. 13.]

Silica is a normal product of the decomposition of the minerals, and has accumulated in relatively large proportions in the soil. It may be present as quartz, amygdaloidal silica, or perhaps as other forms. But undoubtedly there is a distinct tendency, through solution and redeposition,[a] for it to be gradually changed from other forms into quartz. Under arid conditions it is common, as is well known, to find the quartz crystals and crystal fragments with sharp, clean edges, while they are usually more or less rounded in soils from humid areas. But it is astonishing to find how often even in humid areas the quartz does show clean cut, sharp edges, and smooth surfaces with well-marked terminal planes, apparently due to recent deposition from solution. These facts are important, for they tend to negative sometimes expressed opinions that the silica as it is formed from the minerals either as a colloid, or possibly in some other form, coats the minerals and prevents further action of the solvent upon them. Evidence is wanting for the existence of such silica coatings on the minerals of the soil. It is possible that such a coating of silica may take place to some extent, as the experiments of Cushman with colloidal aluminum silicate would indicate; but, if so, it can produce only a retardation of the solvent action, first, since it is itself soluble, and, second, because it would still be possible for more soluble materials slowly to diffuse through it. Microscopic examinations fail to disclose it, such coatings as exist being mainly of ferruginous materials, generally removable quite easily by mechanical means and permeable to water. Moreover, as the silica is generally dissolved from the minerals in the presence of quartz, or other forms of silica, it seems much more probable that the deposition will take place on these latter, increasing their aggregate mass. It must be recognized, however, that silica is transported by ground waters and redeposited sometimes with the formation of siliceous conglomerates or hardpans, though we are unaware of any evidence that this ever takes place in surface soils. The main argument against the formation of siliceous coatings on the minerals is, however, the fact that they are continuously soluble when treated with fresh amounts of water, or when the hydrolized products are removed from the solution.

THE CONTINUOUS SOLUBILITY AND CONSEQUENT HYDROLYSIS OF THE MINERALS.

It should always be kept in mind in considering the action of water upon minerals that we are not dealing with a true solubility effect of the substance, but rather with the extent to which it yields hydrolized products. It is probable that so far as the ordinary silicate minerals dissolve the solute is practically completely hydrolized,

[a] Hayes, Bul. Geol. Soc. America, 8, 213 (1897); Jour. Geol., (3), 5, 319 (1897).

and that therefore the amount of base given to the solution is a measure of the amount of the mineral which has gone into solution. But the presence of the hydrolized products in the solution, especially the basic products, tends to retard further solution of the mineral and if sufficient time were allowed a condition of equilibrium would unquestionably be reached when no further solution could be observed. By removing the solubility products, however, continued solution might be expected. Several series of experiments to test this have been made. A number of rock, mineral, and glass powders have been repeatedly examined by pouring off the supernatant solution and shaking up the residue with fresh portions of distilled water free from carbon dioxide, and all the evidence obtained would lead to the conclusion that solution and hydrolysis would continue until all the base was extracted. Orthoclase, although one of the least soluble of the silicates (even among the feldspars) treated this way steadily continued to give up its basic constituents, as did albite, oligoclase, muscovite, phlogopite, heulandite, soft glass, and hard glass. The effect is much more readily followed, however, in the case of magnesium-bearing minerals, chlorite, serpentine, augite, epidote, and tremolite being the ones actually tested in this laboratory.

Several years ago at the request of one of the authors, Mr. J. F. Breazeale examined the solubility of a number of soils by treating them with water in stoppered vessels for two weeks at a time, pouring off the supernatant solution as completely as possible, adding more water and continuing this process a number of times. The supernatant solutions which were removed were examined by taking their electrical resistance in a standard cell under standard conditions, and also by analyzing for several of the mineral constituents. It was found that the first one or two extractions removed more soluble material than did the subsequent ones, but that after the first few extractions the subsequent ones varied but little in concentration, and, moreover, the extractions from the different soils varied but little from one another.

Another line of investigation which throws light upon the continued solubility of the soil minerals is the raising of water through columns of soil by capillarity, the water being evaporated at the surface. In this way a small but steady accumulation of alkaline material has been secured at the upper surface of the column of soil. The investigation of King[a] is an example of this method.

This method has also been successfully used in this laboratory in the study of the genesis of "alkali" or the accumulation of soluble salts at or near the surface of the soil, a phenomenon common in arid regions. For this purpose a column of soil or sand is arranged with the lower end immersed in a vessel containing a salt solution

[a] Investigations in Soil Management, F. H. King, Madison, Wis., 1904.

and a current of air is blown across the top to hasten evaporation. If, for instance, the outer vessel contains a solution of sodium chloride or sodium sulphate to which pulverized limestone or some other form of calcium or magnesium carbonate is added, then in a few days notable amounts of a mixture of sodium carbonate and bicarbonate can be found on the surface or in the upper parts of the soil column. If the soil contains much organic matter, this is more or less dissolved by the alkali and brought to the surface in a manner similar to that observed as a result of the presence of black alkali under field conditions. Similarly the presence of sodium sulphate in the upper soil layers can be brought about by adding calcium sulphate to a solution of sodium chloride in the outer vessel. It is worth noting, however, that if too rapid an evaporation be induced there will be a more or less complete drying out of the immediate surface of the soil and the "alkali" will be accumulated at some little distance below the surface, a condition commonly observed in nature.

Another method is suggested from the recently published work of Sullivan.[a] The alkali formed by the hydrolizing action of water on the silicate minerals precipitates as hydroxide the base from the salt of a heavy metal, the hydroxyl ions being thus removed from solution. Sullivan used copper sulphate, and we have successfully repeated his experiments substituting silver nitrate. This method is practically the same as having an acid present, that is, the ordinary digestion of the mineral in an acid solution, a common analytical practice.

Another method which is quite effective in removing the products of hydrolysis and thus increasing the solubility of powdered silicates is to pass an electric current through the system, the basic material thus being concentrated at the cathode, and the acid ones, if any, at the anode. Mayençon[b] examined a number of silicate powders by spreading them on a metal plate which was made the cathode, covering with paper and then placing another metal plate upon this as anode. This arrangement to all intents and purposes is a one-diaphragm cell. He found silica accumulated at the anode, and reports that if the latter consisted of silver, zinc, or copper, silicates of these metals were formed. The other elements were accumulated at the cathode, and apparently the process was a continuous one.

Orthoclase paste has been electrolyzed in a one-diaphragm cell by Cushman.[c] A porous porcelain cup was used as a container of the paste, into which was introduced a carbon anode, and a carbon cathode

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[a] Jour. Am. Chem. Soc., **27**, 976 (1905); Economic Geology, **1**, 67 (1905).

[b] Ind. Minerale, Berg-Hüttenm. Zeit., **55**, 333; Chem. Centr., 1896, II, 925.

[c] Bul. No. 92, Bureau of Chemistry, U. S. Dept. Agr. (1905).

was used in the outer vessel. With the passage of the current the hydrolized potassium, as fast as formed, was carried through the walls of the porous cup and accumulated about the cathode in the outer vessel. The electrolytic endosmose of the solution gradually caused the mineral paste in the porous cup to become dry. On remoistening and continuing the process a further but lesser amount of potash was removed. By repeating this process a number of times he finally reached a point where no further potash was removed. This gradual cessation of the yield of potash has been attributed to the formation of colloidal aluminum silicate on the surface of the mineral particles, thus protecting them from further action of the water and also absorbing the potash formed. Regrinding of the residual paste, however, permitted a further extraction of even larger amounts of the base.[a] It is noteworthy that the microscopic examination of soils, while frequently showing the presence of decomposition products on the surface of feldspar grains, always shows the presence of fresh unaltered grains as well, so that Cushman's explanation of the phenomena he observed with rocks would not be entirely applicable to soil conditions. Some four years ago suspensions of mineral and glass powders in water were subjected to the passage of the electric current in this lab-

[a] These experiments have again led to the oft-repeated suggestion of the possibility of extracting potassium commercially from the existing large deposits of feldspar, an obviously desirable thing for agriculture, at least. It seems questionable, however, from the results cited above if any electrolytic procedure can be devised which would be as efficient as some others, as, for instance, the one recently proposed by Rhodin [Jour. Soc. Chem. Ind., **20**, 439 (1901)], who found that by heating together certain proportions of powdered feldspar, lime, and common salt at 900° C. for an hour he obtained about 90 per cent of the potassium originally present in the feldspar as potassium chloride. It will be observed that Rhodin's method is essentially the same as the well-known analytical procedure of J. Lawrence Smith, whereby all the potash is removed without serious difficulty. Ville (Lectures on Agriculture, Massachusetts Society for the Promotion of Agriculture, 1881, p. 87) calls attention to a process used by Ward and Wynants at Brussels, in which the feldspar is mixed with carbonate and fluoride of calcium, heated moderately, and the whole of the potash then extracted by water as the carbonate. This is essentially the original procedure suggested by J. Lawrence Smith for the analytical determination of potash in minerals. For the extraction of potash from leucite see Eng. Pat. 17985 of Aug. 18, 1904. Noteworthy, also, is Pemberton's interesting formation of potash alum from feldspar. [Chem. News, **47**, 5 (1883).]

Furthermore, ground feldspar has itself been shown to be a good artificial soil, as in the classical experiments of Magnus [Jour. prakt. Chem., **50**, 65 (1850)], cited by Johnson [How Crops Feed (1870), p. 160]; and as in the experiments of Headden [Bul. No. 65, Exp. Stat. Agr. Col., Colorado, 1901], who successfully grew an oat crop in it. It has also been suggested as a potash fertilizer, as in the work of Aitken [Trans. Highland and Agr. Soc. (4), **19**, 253 (1887)], who found that with peas it was as efficient as potassium sulphate, and that with oats it was distinctly more efficient. Ballentine (Ann. Rep. Agr. Exp. Stat., Maine, 1889, p. 143) also found that for oats feldspar was a good potash fertilizer, but not as good as potassium chloride. Sabelien [Jids. skr. Norske Landbr., 8, 69 (1901)] and others have reported the results of similar experiments. Dr. A. S. Cushman has suggested to us that in view of the greatly increased facilities and less expensive methods of grinding which have been devised in recent years, and especially wet grinding in the ball mill, ground feldspar might now be economically and in some cases advantageously used as a potash fertilizer.

oratory, using a two-diaphragm cell. The apparatus used was a glass U tube, into the arms of which plugs of various substances were introduced for diaphragms, the powder being placed between them. It was observed that the solution in the cathode arm of the tube increased in volume and was always alkaline. It was suspected, however, from the results obtained with blank experiments in which water alone was added to the tube that the alkalinity might be due to the glass, and as there were other objections to this crude form of apparatus the experiments were abandoned. Recently, however, some of these experiments have been repeated to test the continuous solubility of silicates, using an improved form of apparatus. The one finally adopted consists of two porous cups of unglazed porcelain fitted one inside the other and held in position by a rubber stopper.[a] The outer cup, about 10 centimeters high and about 4.5 centimeters internal diameter, is of the type commonly used in electric batteries. The inner cup was made by cutting off the end of a Pasteur-Chamberland filter tube. The inner cup is fitted with a rubber stopper carrying a block-tin tube bent in a goose-neck form above the stopper, and pierced with two holes immediately below the stopper. These holes are provided to permit the escape and prevent the accumulation of gas in the innermost compartment. The whole apparatus is placed in a beaker or other suitable vessel. Its construction will be readily understood from the accompanying diagram (fig. 1). The tin tube is used as cathode and a strip of platinum foil as anode. The powdered material or soil is placed in the space between the two cups. It has been found advantageous in many cases to distribute the powder or soil through the space by spreading it on absorbent cotton. Before using the apparatus it is cleaned by filling with successive portions of water and running the current through until practically no gas bubbles form. The cotton

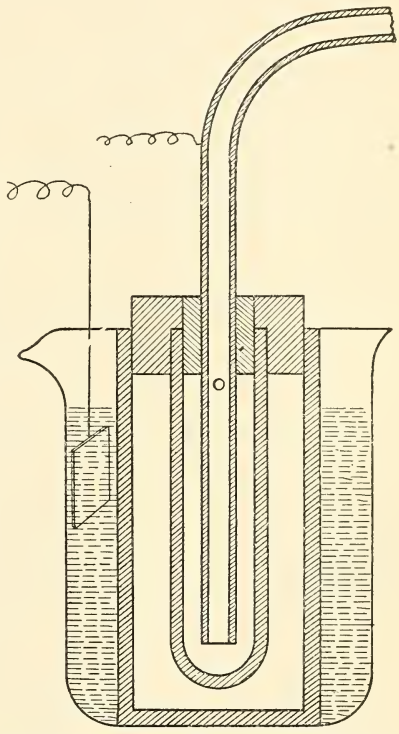

FIG. 1.—Apparatus for the continuous extraction of the water-soluble constituents of minerals and soils.

[a] In some of the work in this laboratory it has been found advantageous to use cylinders of parchment paper instead of unglazed porcelain.

used was, of course, freed from soluble salts. The solution collecting in the cathode compartment by electrical endosmose is carried off by the tin tube and collected in some appropriate vessel, fresh water being added to the anode compartment. It is thus seen that this endosmotic device is to all intents and purposes a method of continuous extraction of the mineral by fresh water, the dissolved and hydrolized products being removed as fast as formed, with the additional advantage that the basic and acidic portions, respectively, are collected in separate compartments.

In one series of experiments six of these cells were placed in a circuit, the current being kept at 40 volts for fourteen days. At the end of this time the resulting solutions, which had been collected from time to time and evaporated to dryness, were analyzed. The voltage was then raised to 80 in order to increase the endosmose and the experiment was continued for eight weeks longer. The cells contained, respectively, apatite, orthoclase, muscovite, hornblende, and serpentine, and Podunk fine sandy loam. The data obtained are as follows:

Showing the extraction by water of the mineral constituents from certain powdered minerals and from a soil.

MINERALS.

Mineral or soil.	Constituent.	Originally present in 1 gram.	Extracted in first two weeks.	Extracted in second two weeks.	Extracted in six weeks more.
		mg.	*mg.*	*mg.*	*mg.*
Apatite	CaO	547	66.3	53.0	147.7
	P_2O_5	403	33.9	31.3	101.5
Orthoclase	K_2O	129	.6	.5	.9
Muscovite	K_2O	96	1.1	1.3	2.3
Hornblende	MgO	281	4.9	2.9	3.8
Serpentine	MgO	395	8.2	5.7	5.5

SOIL.

Podunk fine sandy loam [a]	CaO	3.3	0.8	Bases=1.8 mg. K_2O.	Bases = 1.0 mg. K_2O.
	MgO	5.0	1.0		
	K_2O	11.6	1.5		
	P_2O_5	1.7	.2		

[a] In case of the soil the mineral constituents were extracted from a 5-gram instead of a 1-gram sample.

These results show quite conclusively that even after ten weeks' contact with water the minerals are continuously passing into solution In some cases the rate of solution seems to fall off, and this is probably due not to any actual decrease in the rate, but to a clogging of the pores of the cells and other experimental difficulties. It will be noticed, too, that the lime and phosphoric acid do not appear in the ratio in which they are present in apatite, as shown by the analysis. The normal phosphate ($Ca_3(PO_4)_2$) probably undergoes a decomposition into lime and the acid phosphate $CaHPO_4$.

As might be inferred from the foregoing paragraphs, the rate of solution of the minerals, even when finely pulverized, is very slow. In the course of an experiment samples of powdered glass, orthoclase, albite, and some Podunk fine sandy loam were placed in paraffin cylinders and rotated in a constant temperature bath at 27° C. The resistance of water used was 24,000 ohms. After one day the resistances in ohms of the resulting solutions were as follows: Glass 624; orthoclase, 4,740; albite, 2,728; Podunk fine sandy loam, 6,760. Six weeks later the resistances were as follows: Glass, 140; orthoclase, 940; albite, 1,070; and Podunk fine sandy loam, 3,250. After another three weeks the resistances were: Glass, 82; orthoclase, 735; albite, 1,000, and Podunk fine sandy loam, 2,850. The resistances continued to fall, but the experiment was discontinued. The purpose of this particular experiment was to investigate the possibility of attaining equilibrium conditions within a reasonable length of time, and thus justifying measurements of the absolute concentrations of the resulting solutions.

The desirability of making such determinations has been found to be very questionable, since the results which would be obtained would seem to hold for only that particular sample of mineral. That equilibrium conditions may be obtained with any particular sample is possible, but so far as experimental results have shown it is very doubtful if they have ever been realized. As in the case of phosphates,[a] it has been found that the amount of material which a mineral or mineral powder will yield to a volume of water with which it is in contact for any given length of time is dependent on the relative amounts of solid and solvent present—*i. e.*, on the amount of surface presented for solvent action. This relation has not, however, been found to be a quantitative one. Powdered muscovite which had been kept in contact with water for fourteen months in a sealed paraffin cylinder, when the proportion was 1 gram of powder to 100 c. c. of water, yielded a solution containing 10.4 parts potassium per million of solution, and when the proportion was 1 gram of powder to 500 c. c. of water, yielded 2.1 parts potassium per million, the quantitative relation being apparently very closely approximated; but 1 gram of powdered orthoclase to 100 c. c. of water under the same conditions yielded 2.7 parts potassium per million of solution, while 1 gram of powder with 500 c. c. of water gave 1.7 parts of potassium, and with 2,000 c. c. of water gave 0.5 part potassium per million of solution. Powdered albite, 1 gram of solid to 100 c. c. water, gave 3.7 parts sodium, and with 500 c. c. of water 1 part sodium, per million of solution.

From the foregoing data it appears that equilibrium conditions may be obtained if sufficient time be allowed, and the more quickly

[a] Jour. Am. Chem. Soc., **26**, 885 1454 (1904).

the greater the proportion of solid to liquid in the system. But it also appears improbable that equilibrium conditions have ever yet been attained in laboratory studies on account of the time required, and it seems improbable that any given volume of ground water would ever remain sufficiently long in contact with the soil grains to come into equilibrium with them if other concentration factors did not enter, which factors will be discussed in a later chapter.

THE EFFECTS OF VARIOUS AGENCIES ON THE SOLUBILITY OF THE MINERALS OF THE SOIL.

TEMPERATURE.

So far as we now know, increase in temperature increases hydrolysis.[a] It does not always increase solubility, a familiar case being gypsum,[b] which reaches a maximum solubility at about 37°–40° C. and above 80° C. is even less soluble than in ice water.

Calcium carbonate shaken up with pure water at ordinary room temperatures gives a solution but faintly alkaline, whereas with hot water the alkalinity is very marked. In the same way, all the common silicate minerals give a markedly increased alkaline reaction to the solutions, if the temperature be raised. Since the hydrolysis of the dissolved material is probably complete in these solutions at all temperatures, it follows that the rate of solubility is increased with temperature. Even with those minerals which do not carry an alkali, there is plenty of evidence on record to show an increased solubility with increased temperature, as for instance Wöhler's[c] classical recrystallization of apophyllite on cooling a solution made by boiling the substance in water and Spezia's[d] experiments with the same mineral and with quartz,[e] as well as the work of Dölter[f] cited above. Glass, which is similar to the silicate minerals in composition and many other properties, at higher temperatures goes completely into solution as Barus[g] has shown, being perfectly miscible with water at a temperature between 185° and 200° C. This last observation is especially interesting in this connection, as it shows a remarkable increase in solubility of silica as well as the other products of hydrolysis.

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[a] Th. Madsen, Abhängigkeit der Hydrolyse von der Temperatur. Zeit. phys. Chem., **36**, 290 (1901).

[b] 37.5° C. according to Marignac [Ann. Chim. Phys. (5), **1**, 274 (1874)], and 40° C. according to Hulett and Allen [Jour. Am. Chem. Soc., **24**, 667 (1902)].

[c] Jahresb. Liebig und Kopp, 1847–48, p. 1262.

[d] Jahrb. f. Min., 1895, II, Rep. 242.

[e] Atti Accad. Sci. Turino, **35**, 750 (1900).

[f] Monatsh., **11**, 151 (1890).

[g] Am. Jour. Sci. (4), **6**, 270 (1898).

The effect of alternate heating and cooling, a process to which most of our soils is subjected, at least through a considerable portion of the year, is probably of great importance. The range of the temperature difference in the upper layers of the soil, if not protected by herbage, is probably greater than in the air above, as most soils are known to be good absorbers of the heat rays. The alternation in temperature may be expected to greatly facilitate the process of solution and redeposition with consequent increased rate of crystallization of forming minerals. It also unquestionably tends to break up and prevent the formation of coatings impervious to water, and thus augments the amount of solvent action which this agent is exercising upon the soil particles.

Recognition of the fact that synthetical processes, as well as destructive ones, may be taking place in the mineral species present in the soil, makes necessary some consideration of the influence of temperature. Although our knowledge of this influence in connection with minerals is lamentably meager, it is quite possible that future investigations may show it to have a great importance in determining which minerals would persist under equilibrium conditions, and thus at least to indicate the directions in which changes are to be expected. The phase rule is the one safe guide now available.

With the temperature must be considered also the heat effect and in such studies the principle of le Chatelier[a] must be the guide, which may be briefly stated as regards heat effects, that if heat is added there is increased formation of the components involving the absorption of heat and vice versa.

PRESSURE.

Increase in pressure is popularly supposed to augment the solvent action of water on minerals. This, in some cases at least, may be erroneous, as in the well-known case of ammonium chloride, and as Spezia[b] found in studying the effect of pressure upon the solubility of apophyllite, and as in the investigations of Tammann[c] and of Von Stackelberg.[d] One reason for the popular supposition that increased pressure induces increased solution is undoubtedly the fact that much of the high-temperature work has been done in sealed containers, where the increasing effect due to temperature is large. There is geological evidence to show that solvent action at lower depths in the earth's crust is greater than at the surface; here again

[a] See Bancroft, Phase rule, 1897, p. 4.
[b] Jahrb. f. Min., 1895, II, Rep. 242.
[c] Zeit. phys. Chem., **46**, 818 (1903).
[d] Ibid., **20**, 337 (1896).

probably the increase is to be accounted for as largely due to temperature, but partly no doubt to the increased concentration of the gases in solution, notably carbon dioxide. The general law governing the effect of increase of pressure has been given by le Chatelier[a] and is to the effect that there will be a change in such a direction as will produce the smallest volume; so that if the solid substance and solvent contract on dissolving, solubility will be increased with increase of pressure and vice versa. From the experiments of Barus,[b] working with glasses, it seems fair to deduce that the silicate minerals will in general be more soluble under increased pressure. But we are concerned here only with the soil conditions where the pressure is practically that of the atmosphere, and as solubility effects due to change of pressure are of vanishing importance they need no further discussion.

CARBON DIOXIDE.

Carbon dioxide dissolved in the ground waters is universally recognized as a very important agent in the solution and decomposition of the minerals. In the soil and in the zone of weathering generally its effect is unquestionably due largely to a reduction of the active mass of the hydrates of the hydrolized bases by the formation of bicarbonates. This accounts for the fact that ground waters and soil extracts seldom if ever have an alkaline reaction to litmus or phenolphthalein, although such a reaction is generally shown if the solutions are boiled for a few minutes. That dissolved carbon dioxide may act directly as an acid, thus increasing the solubility, is probable, and the system water, dissolved carbon dioxide, and mineral would then present the problem of the distribution of the base between two acids.[c] But any action of this kind must be rather feeble, since recent researches[d] have shown that carbon dioxide, if it forms an acid at all with water, does so to a very small extent, and the acid formed is but little if any stronger than the silicic acid with which it comes in contact,[e] and, further, the silicates are generally less soluble than the corresponding carbonates. Carbon dioxide, as is well known, dissolves in water to a greater extent than would be expected from Henry's law and forms salts with the hydrates of the

[a] Equilibres, p. 210. See also Nernst, Theoretical Chemistry, trans. by Palmer, 1895, p. 567; Ostwald, Principles of Inorganic Chemistry, trans. by Findlay, 1902, p. 130, and Solutions, trans. by Muir, 1891, p. 61.

[b] Am. Jour. Sci. (4), **6**, 270 (1898); **9**, 161 (1900).

[c] See Mellor, Chemical Statics and Dynamics, 1904, p. 216.

[d] Walker and Cormack, Jour. Chem. Soc., **77**, 5 (1900); Bodländer, Zeit. phys. Chem., **35**, 25 (1900).

[e] Carbon dioxide passed through a solution of sodium silicate does, however, precipitate silica.

base-forming elements. The solubility of the alkali carbonates is pretty well understood now, but the limit of solubility of the alkaline earth carbonates or bicarbonates, when there is an increased pressure of carbon dioxide in contact with the solution, is still undetermined, although the very valuable and interesting papers of Schloesing,[a] Treadwell and Reuter,[b] and Bodländer[c] furnish most important data concerning the solubility of these substances over a fairly wide range of pressures.

That the presence of carbon dioxide in the water does increase its solvent action on the base-carrying silicate minerals is, however, a well-established fact, as witness the experiments of the Rogers brothers,[d] Johnstone's[e] experiments on the micas and olivine, the particularly important work of Mueller,[f] and numerous other researches, practically every investigator in this field of inquiry recognizing its importance.[g] In experiments carried on in this laboratory some powdered minerals were kept in contact for fourteen months with water and certain solutions in paraffin cylinders. Two grams of orthoclase with a liter of pure water yielded a solution containing 1.7 parts of potassium (K) per million, while another solution which had been saturated with carbon dioxide contained 2.5 parts of potassium per million of solution. Two grams of muscovite with a liter of pure water gave 10.4 parts potassium per million, while when treated with carbon dioxide 18.3 parts per million was obtained. Two grams of albite in a liter of pure water gave a solution containing 1.0 part sodium per million, while treatment with carbon dioxide produced but a slight effect, there being 1.1 parts sodium per million of solution. It is certain that in none of these cases had solution finally ceased and definite conditions of equlibrium between the solid and liquid phase been established. Nevertheless, excepting the results obtained with albite, those obtained by treatment with water saturated with carbon dioxide are so much greater than the corresponding results obtained with pure water that no reasonable doubt can exist that the effect of the carbon dioxide was not only to hasten the rate of solution, but actually to increase the solvent action of the water. It has been shown that dissolved carbon dioxide decidedly increases the solubility of the phosphates of calcium,[h] even though the solutions

[a] Compt. rend., **74**, 1552 (1872).

[b] Zeit. anorg. Chem., **17**, 199 (1898).

[c] Ibid., **35**, 28 (1900).

[d] Am. Jour. Sci. and Arts (2), **5**, 401 (1848).

[e] Proc. Roy. Soc. Edinburgh, **15**, 438 (1887–88); **16**, 172 (1888–89); Quar. Jour. Geol. Soc., **45**, 363 (1889).

[f] Untersuchungen über die Einwirkung des kohlensäurehältigen Wassers auf einige Mineralien und Gesteine. Tschermaks min. Mit., **7**, 47 (1877).

[g] See, Peter, Chemical Report of the Minerals, Rocks and Soils of Kentucky, 1854–55, p. 256; Johnson, How Crops Feed, 1884, p. 128.

[h] Jour. Am. Chem. Soc., **26**, 1454 (1904).

be decidedly acid from the presence of free phosphoric acid, in which presumably neither carbonates nor bicarbonates can exist. It would seem, therefore, that while no general satisfactory explanation of the mechanism of the action is yet at hand, it is an empirically determined rule that dissolved carbon dioxide is one of the most important aids to the solvent action of water upon mineral substances.

INORGANIC SALTS.

Since the minerals of the soil are for the most part salts, they should behave as other salts in aqueous mixtures of electrolytes. It may be said that in general they do so behave, although with them special conditions frequently obtain which makes it vastly more difficult to follow the phenomena presented than those usually presented in the laboratory studies which have led to the generalizations or "solution laws" as now understood. Solutions of such substances as calcium hydrate, calcium carbonate, calcium sulphate, the calcium phosphates, iron phosphate, aluminum phosphate, etc., in the presence of various more soluble salts can be studied with comparative ease, as has been shown in several papers from this laboratory. But with the silicates—alumino and ferro silicates—difficulties enter, for the reason that the more familiar solution phenomena is always accompanied by relatively great absorption or adsorption effects, which may be and usually are of a selective character, the basic constituents being more absorbed. For instance, if a neutral solution of potassium or sodium chloride be poured slowly through a column of soil, kaolin, charcoal, absorbent cotton, or similar materials offering a large surface, or be shaken up with a sample of such material the resulting solution is generally distinctly acid, which fact, being attributed to an entirely different cause, has led to a suggested method of estimating soil acidity.[a] The relatively great hydrolysis of the dissolved mineral products introduces another serious complication. Finally, there is the fact that new mineral species may be formed which have about the same order of solubility and other properties as the original mineral possesses.

Thus Lemberg[b] found that by treating leucite ($KAlSi_2O_6$) with a solution containing 10 per cent or more sodium chloride, the corresponding sodium alumino-silicate—analcite ($NaAlSi_2O_6nH_2O$)—was formed to some extent, potassium chloride also being formed. The reverse reaction treating analcite with a solution of potassium chloride and obtaining some leucite was also carried out, and the same investigator[c] has shown that the feldspars and other minerals

[a] Bul. No. 73, Bureau of Chemistry, U. S. Dept. Agr. Proceedings of the Nineteenth Annual Convention of the Association of Official Agricultural Chemists, 1903, p. 114.

[b] Zeit. deutsch. geol. Ges., 28, 537 (1876).

[c] Inaugural dissertation, Dorpat, 1877; Bied. Centr., 1879, p. 568.

undergo the same transformations when treated with solutions of ordinary soluble salts. Lemberg's results are of exceptional value, because his experiments were carried out at ordinary as well as higher temperatures. At higher temperatures in closed tubes Schulten[a] has prepared artificial analcite, and at lower temperatures Friedel and Sarasin[b] have prepared artificial orthoclase, Gonnard[c] has prepared zeolites, and there are a large number of other similar preparations of artificial minerals on record, which show incidentally the saltlike nature of the minerals and their conduct toward other more soluble salts in the presence of water. It is to be regretted that there are not more precise data available as to the stability of the various common rock-forming mineral species in contact with solutions of the more common and readily soluble salts at ordinary temperatures, since such data would be of great value for geological, mineralogical, and soil studies. It offers an attractive field for both phase rule and mass law studies that should be productive of rich results for theoretical and applied chemistry.

Of the published work in this field very little has any value, and that a strictly qualitative one. No equilibrium study of a rigid character has been attempted, the time element generally being ignored, the character of the containing vessels (frequently glass with a greater solubility than the mineral itself) being objectionable, and the relative value of these effects not being recognized.

In a general way it may be said that the ordinary solution laws hold for the complex silicates. Three equal portions of a powdered glass, a potash borosilicate, were put in contact with pure water, a 4 per cent solution of potassium chloride, and a 4 per cent solution of sodium chloride, respectively, and kept agitated at a temperature approximating 27° C. Portions of the solutions, 10 c. c. each, were then withdrawn and titrated with a fiftieth normal (N/50) acid solution. The solution of glass alone required 13.5 c. c. acid solution, that to which potassium chloride had been added required 9.4 c. c. of acid, showing a decreased solubility or "common ion" effect, and that to which sodium chloride had been added required 14.7 c. c. acid, showing an increased solubility which was to be expected from the addition of an electrolyte which did not yield a common ion. None of the solutions, however, had come to equilibrium with the solid phase or phases in contact with them.

Several portions of powdered orthoclase, muscovite, and albite, in the proportion of 1 gram of mineral to 100 c. c. of water freed of dissolved carbon dioxide, were put up in paraffin cylinders. To some of the solutions either potassium chloride or sodium nitrate

[a] Compt. rend., **94**, 96 (1882).
[b] Ibid., **92**, 1374 (1881).
[c] Jahrb. Min., 1884, I, Ref. 28.

was added and the cylinders sealed. The cylinders were kept under as uniform conditions as possible for upward of fourteen months. Orthoclase in water alone yielded a solution which required 3.5 c. c. fiftieth normal (N 50) acid to neutralize a liter of it; with a 1 per cent solution of potassium chloride, 1.7 c. c. acid was required, indicating a depressed solubility, as might be expected as a common ion effect; but with a 1 per cent solution of sodium nitrate only 1.0 c. c. was required, showing an even greater depressed solubility effect where an increase might have been expected. Muscovite in water alone gave a solution requiring 13.3 c. c. of the acid to neutralize a liter, and only 2.5 c. c. acid per liter when the solution contained 1 per cent potassium chloride, but 1 per cent sodium nitrate produced no increase. Albite in water alone gave a solution requiring 8 c. c. of acid to neutralize a liter; 1 per cent of potassium chloride, however, decreased the alkalinity about one-half, and 1 per cent sodium nitrate decreased it to an extent that made a titration impossible. These latter results are similar to those of Dittrich,[a] who observed numerous apparent anomalies in the effects of solutions of various concentrations upon a hornblende granite, the more dilute solutions frequently showing a greater solvent action than more concentrated solutions of the same salts.

For many reasons, because of their wide distribution, the extent to which they occur, and their importance in nature as potash carriers, the feldspars are of particular interest. But they are probably the most unsatisfactory silicates for laboratory studies of solubility effects. On the other hand, the essentially magnesian minerals, with a much greater solubility, are far more readily studied, in spite of the tendency to form basic salts noted on a preceding page. Ten gram portions of a hornblende containing 16.6 per cent magnesium were treated with 250 c. c. portions of pure water, and 4 per cent solutions of potassium chloride, sodium chloride, and sodium nitrate, respectively, in paraffin cylinders, which were shaken continuously for two days and then allowed to settle for twelve days longer. At the end of this time aliquot portions of the several solutions were analyzed to determine the amount of magnesium which had gone into solution. Separate aliquots were titrated with fiftieth normal (N 50) acid, using phenolphthalein as indicator. There was found:

	Water alone.	KCl solution.	NaCl solution.	$NaNO_3$ solution.
	Gram.	*Gram.*	*Gram.*	*Gram.*
Gravimetric	0.0045	0.0083	0.0100	0.0071
Volumetric	.0040	.0086	.0098	.0072

It is thus seen that the three added salts, no one of which gave a common ion, increased markedly the amount of magnesium going

[a] Mitt. Grosch. Bad. geol. Landesanst, **4**, 341 (1901).

into solution as well as the alkalinity resulting from hornblende (essentially $MgSiO_3$).

Flight[a] has studied the action of sodium hydrate and sodium carbonate on feldspar and wollastonite. He found that the carbonate had but a comparatively slight action while that of the hydrate was very great, a thorough decomposition of the minerals being effected. He worked at 100° C. and considered the problem only from the point of view of analytical chemistry, but the results are very interesting in showing the stability of the silicate minerals in the presence of carbonates.

Beyer,[b] Dietrich,[c] and many others have worked on the action of various salt solutions on feldspars, rocks, and soils, the results obtained being more or less indefinite in character, but all showing that there are decided solubility effects produced and that in general these effects are in accord with the indications of the hypothesis of electrolytic dissociation. It is generally recognized that lime salts increase the amount of potassium entering the soil solution, and Manneffe,[d] for instance, has shown that while calcium hydrate is especially effective in this connection, gypsum is much less so. The amount of the effect in any given length of time, however, naturally varies somewhat with different soils. Kalmann and Böcker[e] have shown that with increasing concentration of calcium sulphate the amounts of potassium extracted from some soils increases to a maximum point and then decreases in a manner similar to many solubility curves for pairs of electrolytes. Dusserre[f] in studying the action of various salt solutions on soils found gypsum particularly effective in increasing the amounts of potassium going into solution, while potassium chloride was very effective in increasing the amount of calcium going into solution, and ammonium sulphates markedly increased the amounts of both potassium and calcium in the resulting solution. Further citations seem superfluous in this connection.

It is generally conceded as the result of an immense amount of work, done mainly from an analytical point of view, that acids are particularly effective in increasing the solubility and decomposition of the rock-forming minerals, although some of these latter, as the feldspars, for instance, show a surprising resistance to such treatment.

Iron sulphide, either pyrites or marcasite, is commonly, if not

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[a] Jour. Chem. Soc., **41**, 159 (1882).

[b] Landw. Vers.-Stat., **14**, 314 (1871).

[c] Jahresber. Agr. Chem. (Hoffman), 1862–3, p. 12.

[d] Bul. No. 48 de la Stat. Agron. de l'État à Gembloux, 1891, p. 7; Bied. Centr., **20**, 294 (1891).

[e] Landw. Vers.-Stat., **21**, 349 (1877–78).

[f] Ann. agron. Suisse, **1**, 66 (1900).

generally,[a] a mineral component of soils. It is readily altered by the action of oxygen and water, especially at the surface, but even when comparatively deep seated, being oxidized to the form of sulphate and then dissolved and hydrolized, with a more or less complete precipitation of ferric hydrate and the formation of free sulphuric acid. Mine waters frequently are very acid from this cause, and this laboratory has a number of times had occasion to examine subsoil waters which undoubtedly were carrying free sulphuric acid. Soil investigators are all familiar with the observations of Maxwell,[b] who found sulphuric acid being given off from crevices with steam in the Hawaiian Islands and suggests that this is an important factor in the formation of certain soils.

Several years ago Mr. Thomas H. Means, at that time working in this Bureau, called attention to the formation of a salt incrustation on the surface of some freshly excavated soil at the Howard Reservoir, Washington, D. C., which incrustation was sufficiently acid to "eat holes" in a handkerchief in which some collected specimens had been carried away. An examination showed that the incrustation was in fact ferrous sulphate which was being brought to the surface by the ground water and deposited as a result of evaporation and crystallization, and that the mother liquor contained much free sulphuric acid.[c] It seems altogether probable, therefore, that many, if not practically all, soils are receiving constantly a small amount of sulphuric acid. It is possible, in some cases at least, that the solvent action of this acid on the mineral components of the soil may become important.

It is important, however, to point out that seldom do aqueous extracts of soils show the presence of any free acid other than dissolved carbon dioxide, and that in the majority of cases if the carbon dioxide be expelled, as by heating or passing a neutral gas through the solution, the solution will be found more or less pronouncedly alkaline. It is possible that as a result of selective absorption, which will be discussed in subsequent pages, soils which have been recently or heavily manured with mineral fertilizers may actually contain free mineral acids, as has sometimes been claimed. The classical work of Way[d] especially, and many other observers since, has shown that ammonium salts are more or less completely decomposed in the soil, giving free acid to the soil solution. In this laboratory, Keith has recently found that, in general, potassium salts are decomposed in the same way, some free acid being formed. Seidell has shown that either monocalcium phosphate (the phosphate

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[a] Evans, Min. Mag., **12**, 371 (1900).

[b] Lavas and Soils of the Hawaiian Islands, 1897, p. 12.

[c] See, also, Merrill, Proc. U. S. National Museum, **17**, 88 (1894).

[d] Jour. Roy. Agr. Soc., **11**, 313 (1850).

of superphosphates) or dicalcium phosphate (the phosphate of reverted phosphates) and even some so-called tricalcium phosphates[a] yield a solution with a markedly acid reaction, and Hurst has shown that ferric and aluminum phosphates or the products formed by the precipitation of phosphoric acid with iron or aluminum salts, even when the latter are in excess, yields an acid solution, the latter work being in harmony with the researches of Lachowitz,[b] Schneider,[c] and others. When one considers, however, the relation of the amounts of the usual fertilizer applications to the amounts of soil with which they are brought in contact, it seems improbable that resulting acid effects are of much importance except in very special cases.

ORGANIC COMPOUNDS.

It is quite commonly held that certain acids—humic, ulmic, crenic, apocrenic, etc.—exist in soils and have in the aggregate an enormous solvent action on the minerals. This seems to be quite improbable, however, on a close analysis of the known data. The existence itself of these acids has never been satisfactorily demonstrated. Much of the organic matter in soils is dissolved by aqueous solutions of alkalies and is reprecipitated by mineral acids, a general characteristic of organic acids, it is true, but one also shared by many other forms of organic matter, for instance cellulose. No satisfactory description of the physical or chemical properties of these supposed acids, their salts, or characteristic derivatives have been recorded. In this laboratory the organic matter from a large number of soils of widely different origin and type characteristics has been extracted by aqueous solutions of ammonia, potash, or soda. These extracts have been carefully filtered through Pasteur-Chamberland tubes to exclude any suspended solids, and then acidified with hydrochloric acid, the precipitated organic material thoroughly washed and dried in thin layers at room temperature. In no case did any of these precipitates thus obtained yield an aqueous solution which was acid to a sensitive litmus solution. In practically every case where they were moistened and pressed on sensitive litmus paper, the latter showed a greater or less reddening. This reddening, however, can not be regarded as indicative of the presence of acid (or hydrogen ions) in the organic precipitates, but was more probably a purely absorptive phenomenon, as will be shown in the following chapter. The analyses of these various precipitates showed a range in the percentage of carbon greater than that required by the generally accepted formulas for the soil acids cited. Even

[a] Warington, Jour. Chem. Soc., **26**, 983 (1873).
[b] Monatsh., **13**, 357 (1892).
[c] Zeit. anorg. Chem., **5**, 84 (1894); **7**, 386 (1894).

granting the existence of these supposed acids it is obvious that since they do not dissolve to an extent sufficient to be detected by sensitive indicators, they can not exert much solvent effect *as acids* on the soil minerals. That these supposedly acid organic materials may have an important rôle as carriers of bases is, however, quite probable, but due to their remarkable absorptive or adsorptive powers and not to acid properties.

The high absorptive capacity enables the organic matter of the soil, or soil layers rich in organic matter, especially when moist, to accumulate unusual amounts of carbon dioxide, and it seems possible that the solvent action of the dissolved carbon dioxide may readily account for such observations as that of Storer[a] who describes a heavy layer of soil unusually rich in organic matter immediately over a layer quite white in color and unusually free from iron, and that the soil about decaying roots is frequently lighter in color owing to a more or less complete removal of iron.

VITAL AGENCIES.

That acids are formed in the soil and *may* sometimes accumulate in sufficient quantity to make the soil solution distinctly acid can not be doubted. Molds, fungi, bacteria of various kinds,[b] possibly enzymes[c] and various organisms are constantly at work in arable soils modifying both the organic and inorganic substances present and in many cases we know that acids are among the products of their activities.

Roots of growing plants are often supposed to be of great importance in this connection, the idea being that they excrete acids both organic and inorganic, which increases the solvent action of the soil solution on the minerals of the soil. It is true that plants growing in artificial water cultures made up from the ordinary salts of the laboratory frequently do leave the nutrient solution somewhat acid. But this does not necessarily prove that acids are excreted from the roots as it is altogether probable that the roots can and do exercise a selective absorption among the constituents or resulting ions of the

[a] Agriculture, 1887, Vol. I, p. 131.

[b] See, for instance, Muntz, Compt. rend., **110**, 1370 (1890); Lipman, New Jersey Stat. Rep. (1903), p. 217; Chester, Bul. No. 66, Delaware Exp. Stat. (1904); Hansen, Centr. Bakt. Par., 14, 545 (1905).

[c] It has been shown by repeated tests in this laboratory that many (but by no means all) soils shaken up with an alcoholic solution of guaiac, give the blue color characteristic of oxidases. That the color was produced by enzymes, however, is by no means certain, though the presence of no other oxidizing substances which give this reaction could be detected. Woods [Bul. No. 18, Bureau of Plant Industry, U. S. Dept. Agr., 1902, p. 20] has shown in his studies on the mosaic disease of tobacco the probable presence of a peroxidase in the soil. We have not ourselves observed the presence of peroxidases, but too few cases have been examined to justify any generalization.

salts, taking up the bases and leaving the acids,[a] and there is no special difficulty in preparing a nutrient solution, one in which the added salts are mainly nitrates, for instance, which will become alkaline as the growth of the plants proceeds. The evidence generally advanced as conclusive of the exudation of acids from roots is that afforded by the classical experiments of Sachs[b] in producing etched figures on slabs of marble and similar materials against which growing roots have been pressed. But the experiments of later investigators, notably Czapek,[c] who found no etching on slabs of aluminum phosphate (which substance is not attacked by dissolved carbon dioxide, although readily attacked by most inorganic and organic acids), and Kossowitch,[d] have shown that these effects so far observed can all be most readily explained as due to the action of carbon dioxide, which Spring[e] has shown acts most vigorously at surfaces of contact. Pfeffer,[f] in an authoritative and most interesting résumé of this subject, concludes that, while lichens and perhaps even some of the higher plants may excrete from their roots acids other than carbon dioxide, there is no satisfactory evidence that this is characteristic of the higher plants, and that the explanation that the effects under discussion are produced by carbon dioxide is supported by the greater weight of evidence. Whether roots do or do not excrete acids they do at least indirectly have a great importance in promoting the solution and decomposition of the minerals of the soil.[g] Dead roots, leaves, twigs, and other similar materials naturally are operative in a similar manner.[h] Earthworms,[i] crawfish, ants, and various insects and other more or less similar organisms have a decided effect on the soil, partly by a mechanical movement or transportation of soil particles, but very largely as a result of their excreta, earthworms being particularly important, according to Auchald,[j] who in summarizing the work of Dusserre[k] states that the excreta of earthworms contains more nitrogen and more easily oxidized nitrogen compounds than the original soil; that the phosphoric acid is more readily soluble, and that the amount of calcium carbonate is increased in the soil after excretion by the worms.

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[a] See Report No. 71, U. S. Dept. Agr., 1902, p. 67; Storer, Agriculture, 1887, Vol. I, p. 192.

[b] Experimental-Physiologie der Pflanzen (1887), p. 189.

[c] Jahrb. wiss. Bot., **29**, 321 (1896).

[d] Ann. de la Sci. Agron., (2), **1**, 220 (1903).

[e] Zeit. phys. Chem., **4**, 658 (1889).

[f] Physiology of Plants, 1900, trans. by Ewart, Vol. I, p. 171 et seq.

[g] See, for instance, Sestini, Ann. Agron., **25**, 399 (1899), and Landw. Vers.-Stat., **54**, 147 (1900).

[h] Denaro, Gazz. chim. ital., **16**, 328 (1886).

[i] Darwin: The Formation of Vegetable Mold 1898, p. 230 et seq.

[j] Jour. Agr. Prakt. (3), 1902, p. 700.

[k] Annuaire agricole de la Suisse, **3**, 25 (1902).

The precipitation of dust and atmospheric gases, the effects of tillage, the various activities of man and other animals, while of enormous importance in their effects upon the soil, act more or less indirectly, as they affect the soil solution and need not be considered more specifically here.[a]

ABSORPTION.

ADSORPTION.

The changes which take place in soils and soil solutions are quite varied in character, and it is sometimes difficult to ascribe any change to any one specific cause. The first and most important change is, of course, solution of the mineral matter by water. In most cases the salts which are dissolved are so weak that hydrolysis follows, and there is a change in the material in solution. It is quite possible to have also a change in the mineral itself if there are present salts of another base or acid in the solution. Such a change would be represented in the case of an alteration from orthoclase to albite by the equation

$$KAlSi_3O_8+NaCl=NaAlSi_3O_8+KCl.$$

The above changes have been discussed at length in preceding pages. Another general change is adsorption, which follows the allied phenomena of solution and hydrolysis. By adsorption is meant the phenomenon of the difference existing between the concentration or density of the liquid film adjacent to a bounding medium and the concentration or density of the mass of the liquid. Differences in concentration or density between the mass of the liquid and the surface portions have been observed at both solid and gaseous bounding surfaces. Zawidski[b] proved that the foam formed by blowing air through an aqueous solution of hydrochloric acid or acetic acid to which a little saponine had been added was more concentrated than the original solution, and Miss Benson[c] found that the foam of aqueous amyl alcohol was richer in alcohol than the original solution. Spring[d] has shown that at bounding surfaces of dilute solutions, such as with bubbles, chemical action is increased.

There are several important physical changes accompanying a great increase in the surface of a liquid. It was early shown by Pouillet[e] that there is a temperature increase when finely-divided powders.

[a] See Merrill, Rocks, Rock Weathering, and Soils, p. 292 et seq; Van Hise, Monograph XLVII, U. S. Geol. Survey, 1904, p. 427; Shaler, Twelfth Annual Report, U. S. Geol. Survey, Action and Reaction of Man and the Soil, 1890–91, p. 329.

[b] Zeit. phys. Chem., **35**, 77 (1900).

[c] Jour. Phys. Chem., **7**, 542 (1903).

[d] Zeit. phys. Chem., **4**, 658 (1889).

[e] Ann. Chim. Phys., **20**, 141 (1822); Gilb. Ann., **73**, 356 (1823).

both inorganic and organic, become wet with water, alcohol, ethyl acetate, and oil. In the case of water Jungk[a] found that above 4° C. there was an increase in temperature, and below 4° a decrease in temperature. This result is attributed to an increase in density at the surface of the powder, which above 4° would tend to increase the temperature of the mass of the liquid and below 4° would decrease the temperature. Meissner,[b] however, has more recently found an increase in temperature at 0° C. Lagergren[c] has calculated the pressure of the water at the surface of a solid consequent upon the increase in density, and finds a pressure upward of 6,000 atmospheres. A change in density has also been noted by Spring,[d] who found that the amount of water required to fill the spaces of a given mass of sand was greater than would be expected if it were merely a phenomenon of occupying the air spaces. This phenomenon has been ascribed to an increase in the density of the water in the water layer at the surface. It may be noted, in passing, that this fact points to a source of serious error in the usual method of determining the density of powders and porous bodies by the addition of a liquid of known density to occupy the spaces. A substance in the form of powder would show a greater apparent density than the same substance in mass, and experiments by Rose[e] indicate that the degree of division affects the density. Gold in the form of a very fine powder gave a density as high as 20.71, while in the form of plates it gave only 19.49. Pure heavy spar shows a density of 4.48, while barium sulphate obtained by precipitation has a density of over 4.52. This increase in density at the surface of a liquid is in harmony with the results of Bunsen,[f] who found that at the surface of glass the pressure under which a film of water stood was very many times the ordinary pressure. This enormous increase of pressure was proved by the increased solubility (over 2,000 fold) of carbon dioxide in the water. Another explanation may be offered, however, namely, that the glass gave up part of its alkali to the water, which then combined chemically with the carbon dioxide.

Another phenomenon sometimes confused with adsorption is the ability of certain solid substances to absorb some materials from solution and to leave others unaltered. This power of absorption is selective, i. e., the solid material has the power of preferring some substances to others. This power is certainly analogous to the selective ability of water to dissolve (for example) barium nitrate

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[a] Pogg. Ann., **125**, 292 (1865).
[b] Wied. Ann., **29**, 114 (1886).
[c] Bihang till K. Sv. Vet.-Akad. Handl., **24**, Afd. II, No. 5 (1898).
[d] Mem. Soc. Geol. Belge, **17**, 13 (1903).
[e] Pogg. Ann., **73**, 1 (1848); **75**, 403 (1848).
[f] Wied. Ann., **24**, 385 (1885).

and to leave barium sulphate practically undissolved. In the case of absorption by a solid there is formed a solid solution.[a] But the rate at which a solid is penetrated by a substance soluble in it—or, in other words, the rate of solution—is very slow, and depends directly on the amount of surface exposed. Consequently the absorbed material will be concentrated in the surface of the solid, and the phenomenon appears to be practically indistinguishable from adsorption. Theoretically, the only method of distinguishing these two phenomena, seems to be based on the fact that the time required to wash away the adsorbed material is very much less than the time required to wash the solute from the solid solution. In the latter case, when water is added, there is a slow change to acquire the proper distribution ratio of the solute between solid and liquid solvents. As there is no hard and fast method of distinguishing between these two phenomena, we shall call them both absorption and restrict the term adsorption to the change of concentration or density of a liquid at the surface of a solid. The changes due to an adjustment of the equilibrium consequent upon a change in the mineral itself which was spoken of above, will not be termed absorption, because it is possible to distinguish, by chemical analysis of solid and liquid phases, between this phenomenon and that of adsorption or absorption.

ABSORPTION OF GASES.

The absorption of gases by solids has been the object of much experimental work, and it will be sufficient here to point out the magnitude of the absorption and the effect of changes of pressure and temperature. From the available data collected by Pfeiffer[b] it follows that equal changes in pressure produce about equal changes in the amount of gas absorbed. This holds fairly well for the absorption by different kinds of carbon. The absorption of hydrogen by palladium has been studied quite recently by Hoitsema.[c] In this case increase of pressure is accompanied by an increase in the amount of gas absorbed, but the governing law is still unknown. Increase of temperature caused a decrease in the solubility in the cases studied. Pfeiffer[d] found that the absorption of ammonia by charcoal decreased about one-half on heating from 0° to 70° C., while the absorption of cyanogen decreased about one-fourth for the same temperature limits. The case of the absorption of hydrogen by palladium follows the same rule. The results of Hoitsema[d] are quite interesting,

[a] It must be specifically understood that the term "solid" is not here used with the restricted meaning proposed by Tammann—that is, meaning crystalline substances alone.

[b] Über die Verdichtung von Gasen durch feste Körper; Inaug. Diss., Erlangen (1882).

[c] Zeit. phys. Chem., **17**, 1 (1895).

[d] Loc. cit.

and present some phenomena for which no satisfactory explanation has been offered.

Reichardt and Blumtritt[a] determined the amount of gas absorbed by various substances by exposing them to the atmosphere. The following table gives some of the data:

Absorption of atmospheric gases by various substances.

Substance.	Gas in c.c. per 100 grams.	Per cent by volume.		
		Nitrogen.	Oxygen.	CO_2.
Charcoal, air dry	164	100	0	0
Peat	162	44	5	51
Garden soil	14	65	2	33
$Fe(OH)_3$, air dry	375	26	4	70
Fe_2O_3 ignited	39	83	13	4
$Al(OH)_3$, air dry	69	41	0	59
Alumina, dried at 100° C	11	83	17	0
Clay	33	65	21	14
Clay, moistened	29	60	6	34
River silt	40	68	0	32
Magnesium carbonate	729	64	7	29
Gypsum, pulverized	17	81	19	0

The table shows that nitrogen is absorbed to a much greater extent than is oxygen, showing the selective absorptive power of substances. Porous charcoal absorbs enormous quantities of gases from putrefying animal matter, and soils have the power of absorbing almost continuously the odors from excreta. The absorption of gases by the various constituents of the soil has been the object of experiments by Ammon,[b] who found that water vapor and ammonia gas were all absorbed to a greater or less extent by sand, aluminum silicate, calcium carbonate, ferric hydroxide, gypsum, clay, and humus. Scheermesser[c] has stated that the amount of carbon dioxide absorbed by a dry soil is proportional to the amount of ferric oxide present, which would appear to be a generalization based on too restricted a number of observations.

ABSORPTION OF SOLUTES BY SAND.

From the point of view of soil chemistry the absorption of materials from solutions by solid substances is probably of more importance than the absorption of gases, although the latter is undoubtedly important in the case of carbon dioxide. The experimental work in this subject is almost altogether confined to experiments of a qualitative nature because of the extreme difficulty in reproducing conditions. The absorption of salts by sand was studied by Way,[d] who found that at the surface of the sand particles there was an

[a] Jour. prakt. Chem., **98**, 476, (1866).
[b] Bied. Centr., 1879, p. 511.
[c] Inaug. Diss., Jena, 1871; ref. Chem. Centr., 1871, 462.
[d] Jour. Roy. Agr. Soc., **11**, 313 (1850).

excess of the basic substance. The author distinguished between this phenomenon and that of capillarity, which would, he claims, be exerted on the salt and not individually on the acid or basic parts. He also found that clay had the power of absorbing potash from an aqueous solution, a phenomenon which may have been due to the formation of aluminates or silicates or both, which were then concentrated at the surface of the unchanged clay. In his paper Way cites several previous experiments which are well worth mentioning here. The absorptive power of sand has been known for centuries. The removal of the salts from sea water by passing through sand filters or earth was practiced in Bacon's day. Dr. Stephen Hales announced to the Royal Society in 1739 that the first portion of sea water passed through stone cisterns was pure. Berzelius filtered salt solutions through sand and found that the salt content was completely removed. Matteucie, however, determined the concentration of salt in the solution after passing through successive filters and found the concentration to be successively smaller. That sea water and impure drinking water could be purified by passing through sand filters has been known since the time of Aristotle.[a]

ABSORPTION OF SOLUTES BY PAPER.

The effect of such an absorbing medium as paper has been the object of numerous experiments. Schönbein,[b] the first experimenter on the absorption by paper, dipped strips into different solutions and determined the ratio between the height to which the water rose and the height of the solution in the paper. As paper has more absorbing effect on the salt or organic substance, the rate at which that substance rose would be much less than that of the water. Red litmus solution containing very little excess of free acid was absorbed by paper, and the upper portions of the wet paper were found to have become blue, due to the absorption of the acid. Goppelsröder[c] has used the result of this investigation as a basis for the separation of different dyes. From several interesting experiments one example should be cited. Making use of the different absorptive power of paper for different dyes, he succeeded in separating out a rose-red-colored substance, probably fuchsine, from commercial azuline, the azuline losing its violet tint and acquiring a purer blue color. It was observed by Bayley[d] that when drops of certain solutions fell on filter papers there was a separation into a water ring surrounding

[a] See Sachsze, Lehrbuch der Agriculturchemie, 1888, p. 146.

[b] Verhandlung d. Naturforsch. Ges. in Basel, **3**, 249, (1861–63); Pogg. Ann., **114**, 275 (1861).

[c] Ibid., **3**, 263 (1861–63); Mitteil d. techn. Gewerbemuseums, Wien (1889).

[d] Jour. Chem. Soc., **33**, 304 (1876).

a solution more concentrated than the original solution. He further observed that with increasing dilution the amount of separation became greater and that increase of temperature and looseness of the texture of the paper increased the mobility of the solute, and hence lowered the absorptive effects. Lloyd[a] has determined the relative separations of solutions of different salts, and finds that while with sodium chloride no separation was observed, sulphuric acid and solutions of ferric sulphate, and of salts of silver, lead, and mercury suffered more or less separation into water and a stronger solution. The same method has been employed by Trey[b] more recently in the qualitative separation of cadmium from copper. The solution containing the mixture is made alkaline with excess of ammonia and diluted until the blue color is scarcely visible. Several drops of the solution are allowed to spread into a filter paper. On holding the wet paper in ammonium sulphide vapor three rings are distinguished—the outer water ring, which has traveled ahead of both metals; the yellow ring of CdS, the cadmium having traveled faster than the copper, and in the center a black circle of mixed copper and cadmium sulphides. In these experiments it has been noticed that usually water moves faster than the solution, and hence if a solution be passed through a filter the first portion will be generally less concentrated than the main portion. This has actually been found to be the case by Vriens,[c] who passed dilute nitric acid through several filter papers and found the absorption of acid (measured by decrease in concentration) to be proportional to the number of filter papers used.

The degree of absorption has been ascribed to the change in surface tension due to the presence of the solute. Quoting from J. J. Thompson:[d]

> If the surface tension is increased by the addition of the salt there will be less salt per unit volume in the film than in the liquid in bulk, while if the surface tension is diminished by the addition of salt there will be more salt in unit volume of the film than in unit volume of the rest of the liquid. We saw that the surface tension of solution in contact with a solid diminished as the strength of the solution increased; thus if we had a film in contact with a solid there would be more salts in unit volume of the film than in unit volume of the bulk of the liquid; if we dipped, for example, a piece of filter paper in such a solution, the solution in the filter paper would be stronger than in the rest. Or, again, if such a solution were to flow through a capillary tube, the salt would have a tendency to flow to the sides, so that the more quickly moving fluid at the center would get weaker and weaker. Many experimental illustrations of this could be given; one of these is an experiment tried by Doctor Monckmann and myself at the Cavendish Laboratory, in which a deep-colored solution of potassium permanganate emerged almost colorless after trickling through finely divided silica. Again, if a piece of filter paper be dipped into a colored solution of a salt, such as potassium permanganate, unless the salt has a very strong affinity for the water, the solution

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[a] Chem. News, **51**, 51 (1885).
[b] Zeit. anal. Chem., **37**, 743 (1898).
[c] Zeit. phys. Chem., **31**, 230 (1899).
[d] Applications of Dynamics to Physics and Chemistry (1888), p. 191.

after rising some height in the filter paper becomes colorless. If a small quantity of paraffin oil be mixed with water, the surface tension of the solution against a solid is greater than that of water, and such a solution will increase in strength when it flows through finely divided silica.

Selective absorption can be well illustrated with aqueous solutions of dyes, as the following experiments will show. Three solutions were prepared. The first contained methylene blue, although it was also found that malachite green or several other dyes would serve nearly as well. The second solution contained eosin or its sodium salt, the latter being preferred on account of its ready solubility. The third solution was a mixture of the first and second. A blank of pure water was also used. Four strips of ordinary white blotting paper, free of sizing, were prepared, the strips being as nearly identical as possible

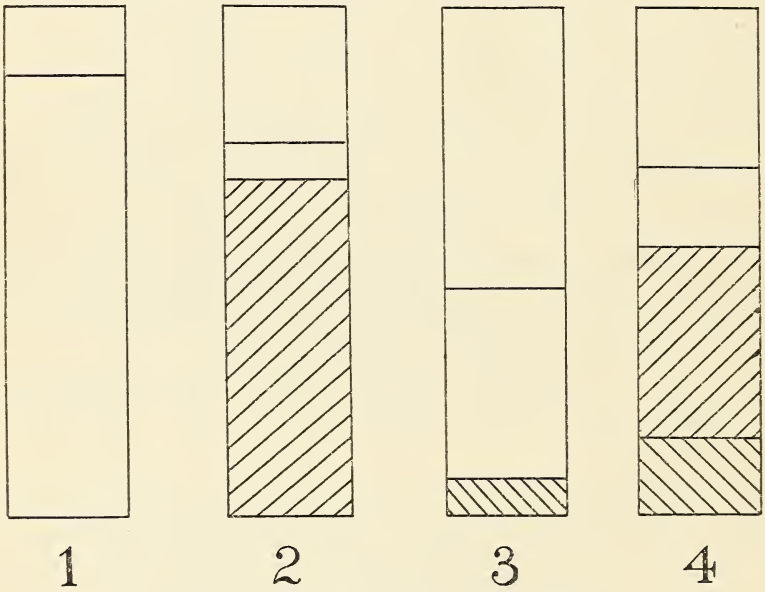

FIG. 2.—Illustrating rise of dye solutions in paper.

in all respects. The four strips were arranged vertically and lowered one into each of the solutions described above and into pure water, so that the lower edges of the slips just touched the surfaces of the solutions. The contacts were made as nearly as possible at the same instant.

At the end of any selected time it was observed that the height of the capillary rise was greatest in the slip in contact with pure water, as shown by slip 1 in the accompanying figure (fig. 2). The rise was less in the slip in contact with the eosin and the dye had not risen quite as far as the water had gone, the dye obviously exercising a retarding effect on the capillary movement of the water, as shown by slip 2. In the case of the solution of methylene blue the water had risen to a

much less height and the dye to a very slight height indeed, as illustrated by slip 3. Slip 4 represents the results from the mixed solution of methylene blue and eosin, and it will be observed that while neither the water nor the eosin rose as high as with the solution of eosin alone, the methylene blue had risen decidedly higher than with the solution of it alone. It is obvious, therefore, that there is a great difference, in degree at least, in the effect produced by different kinds of organic matter and that they mutually affect one another to a considerable degree. Precisely similar results were observed with other absorbing materials, such as unglazed porcelain, tubes filled with absorbent cotton, and tubes filled with various soils, the effects being usually even more pronounced in the case of soils than with the other absorbent materials used. As in the experiments of Thompson, cited above, the presence of still other soluble substances, such as alcohol or mineral salts, very sensibly modified the degree of the separation of the dyes by the soils or other absorbents.

The movement of solutions through paper has been made a velocity study. Following are some experiments on the movement of solutions of sodium eosin through paper. Strips of blotting paper were cut 1 inch wide and about 8 inches long, and different lengths were scaled off by marking lightly with a pencil. The ends of the strips were immersed in this solution, and the height to which the solution had arisen at different times was read off. In this case there were two heights—the height to which the water rose and the height colored by the dye.

Rise of distilled water and sodium eosine solutions in blotting paper.

Time.	Height of pure water.	Sodium eosine solution, 5.82 grams in 1 liter.		Sodium eosine solution, 11.64 grams in 1 liter.	
		Height of colorless solution.	Height of colored solution.	Height of colorless solution.	Height of colored solution.
Minutes.	*Inches.*	*Inches.*	*Inches.*	*Inches.*	*Inches.*
0.0	0.0	0.0	0.0	0.0	0.0
.25	.59	.5	.42	.46	.41
.5	80	.67	.55	.66	.59
.75	.94	.84	.65	.79	.70
1	1.06	.99	.75	.91	.81
1.25	1.16	.....	.....	.....	.....
1.50	1.25	1.16	.95	1.09	.95
1.75	1.34	.....	.....	.....	.....
2	1.40	1.31	1.05	1.21	1.06
2.5	1.54	1.46	1.16	1.36	1.16
3	1.67	1.58	1.26	1.50	1.27
4	1.90	1.79	1.44	1.66	1.44
5	2.10	1.99	1.60	1.85	1.56
7	2.45	2.35	1.85	2.16	1.81
10	2.86	2.75	2.16	2.52	2.10
13	3.16	.....	.....	2.85	2.38
16	.....	.....	.....	3.13	2.59
20	3.84	3.72	2.97	3.45	2.84
25	4.21	4.40	3.46	3.77	3.16
30	4.52	.....	.....	4.10	3.38
40	5.09	4.92	3.89	4.58	3.80
50	5.52	.....	.....	.....	.....
60	6.00	.....	.....	.....	.....

In figure 3 curve 1 shows the height to which pure water rose at different times. Curve 2a shows the height which had become wet, and curve 2b shows the height which was reddened. The original solution in this case contained 5.82 grams per liter. A strip of paper was dipped into a solution containing twice the amount of the dye per liter. Curve 3a represents the rate at which the paper became wet, and curve 3b the rate at which it became red.

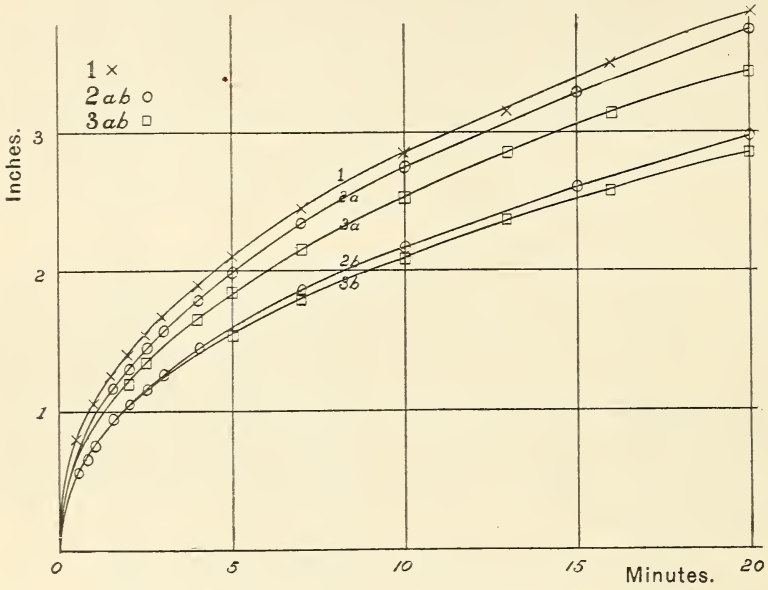

FIG. 3.—Curves showing the rate at which dye solutions rise in paper.

It will be seen from the curves that the rate at which water travels is decreased by the presence of sodium eosine, and that the greater the concentration the less is that rate. The separation of water and eosine is also more marked for the lower concentration. These curves were also found to be parabolic, i. e., to have an equation of the form

$$y^n = kt,$$

an equation which is purely empirical, but holds remarkably well for the observed data. In this equation y is the height, t is the time, and n and k are constants depending on the temperature, the solution used, and the material through which the liquid passes.

The effect of a salt, potassium chloride, on the rate at which eosine is absorbed was next determined at 25° C.

Rise in blotting paper of potassium chloride solution and of a solution containing potassium chloride and sodium eosine.

KCl, 50 grams per liter.		KCl, 50 grams per liter. Sodium eosine 5.829 grams per liter.	
Time.	Height of rise.	Height of colorless solution.	Height of colored solution.
Minutes	*Inches.*	*Inches.*	*Inches.*
0.0	0.0	0.0	0.0
.25	.55	.....	.....
.50	.80	.7	.3
.75	.96	.....	.....
1	1.08	1	.4
1.50	1.30	1.2	.5
2	1.46	1.37	.55
3	1.77	1.67	.65
4	2	1.9	.7
5	2.22	2.1	.8
7	2.54	2.43	.9
10	2.97	2.82	1
13	3.30	3.15	1.05
16	3.60	3.44	1.12
20	3.97	3.77	1.2
25	4.37	4.10	1.3
30	4.60	4.44	1.38
45	.....	5.17	1.55

These results are plotted in figure 4. It is quite evident that the effect of the potassium chloride is to decrease markedly the rate at which the dye travels through the paper. We have thus shown

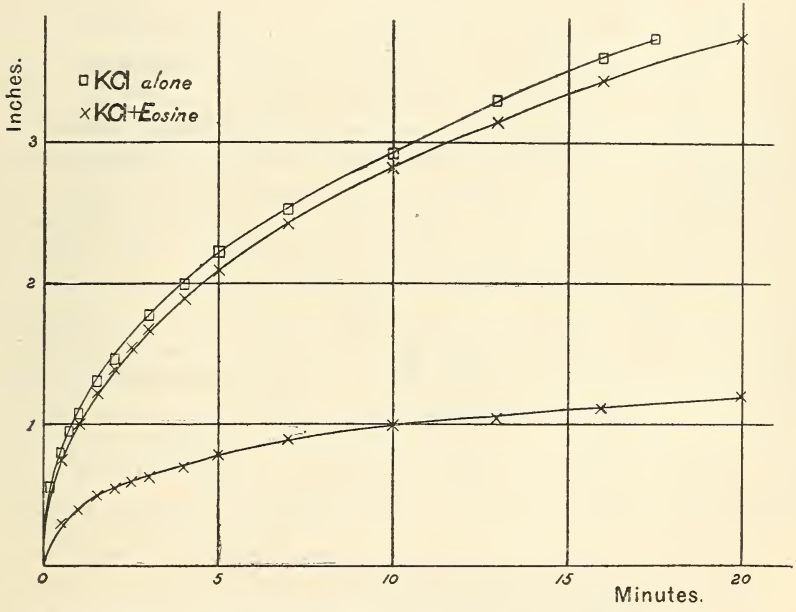

FIG. 4.—Curves showing the effect of eosin on the rate at which KCl solution rises in paper.

that the solutes do not act independently of one another, but the nature and extent of this dependence have not yet been determined.

ABSORPTION OF SOLUTES BY CARBON, SILICA, KAOLIN, ETC.

It has long been known that not only paper, but also such a material as carbon black, has the power of removing dissolved material from solutions. The decolorizing action of wood carbon was discovered in 1791 by Lowitz.[a] The greater absorbing power of animal charcoal was discovered later by Figuier. Payen[b] showed that not only does carbon in a fine state of division remove coloring matter, but also lime is removed. The phenomenon of decolorization was ascribed by Graham[c] to the power possessed by the carbon of concentrating on its surface the coloring matter—a purely mechanical explanation. Carbon has been found by Graham to absorb the metal from many compounds, indicating that carbon not only acts mechanically, but also chemically. Graham found that the metal was removed from solutions of lead acetate, lead nitrate, copper sulphate, copper ammonium sulphate, silver nitrate, silver chloride in ammonia, lead oxide in potassium hydroxide, and zinc oxide in potassium hydroxide. In the case of silver nitrate, metallic plates of silver were visible in the carbon. Oechsner de Conick[d] has shown that when solutions of salts of the heavy metals are filtered through charcoal the metal is more or less retained and the filtrate is acid, a quantitative separation of chlorine as hydrochloric acid from ferric chloride being readily made in this way. Weffen[e] has shown that carbon which has already acted upon ferrous sulphate solution will decompose more of either mercuric chloride or copper sulphate than in the pure condition. Birnbaum and Bomasch[f] found that boneblack absorbs a small amount of ammonia from ammonium salts, and that in other cases the acid and basic portions were absorbed in unequivalent proportions. Qualitative experiments by Lieberman[g] have shown that not only does the concentration change, but also the acidity or the basicity. The following salt solutions passed through animal charcoal gave acid solutions, some of which on distillation gave the free acid: The barium salt of the acid formed by oxidizing glycerin with chromic acid, barium formate, sodium acetate, lead acetate, calcium glycollate, zinc lactate, ammonium oxalate, sodium-potassium tartrate, sodium borate (previously alkaline); trisodium phosphate (previously very alkaline), disodium phosphate, ferrous sulphate, copper sulphate, silver nitrate, and potassium acetate. The following aqueous salt solu-

[a] See Ostwald, Stoechiometrie, 1891, p. 1093.
[b] Ann. Chim. Phys., **21**, 215 (1822).
[c] Pogg. Ann., **19**, 139 (1830).
[d] Compt. rend., **130**, 1627 (1900).
[e] Ann. Phys. Chem., **55**, 241 (1845); **59**, 354 (1846).
[f] Ding. Poly. Jour., **218**, 148 (1876).
[g] Wien. Akad. Ber., **74**, 331 (1877).

tion, however, showed no change of alkalinity or acidity, but the concentrations were less after passing through the carbon: sodium chloride, nitrate, and sulphate; potassium chloride, iodide, bromide, cyanide, sulphocyanate, and sulphate; calcium chloride, and barium chloride and nitrate. In the case of morphine acetate and caffein citrate the first percolates contained none of the solute, but after a time the free acids came through. When carbon black is shaken with an aqueous solution of hydrochloric acid, Kelberin,[a] working under Ostwald's direction, has found that there is a perfectly definite distribution ratio, for the results could be duplicated within a fraction of 1 per cent. The equilibrium ratio depends on the quantity and concentration of the acid for keeping the amount of carbon and acid constant, and varying the amount of water the amount of acid absorbed by the carbon was found to vary inversely with the mass of water. Kroeker,[b] who studied the relation between the absorption and the time of contact, the quantity of carbon, and the concentration of the solution, found that the distribution ratio between carbon and the liquid solvent is not constant, but decreases with increasing solution concentration. Schmidt,[c] using van Bemmelen's data,[d] has sought to show that the distribution ratio of potassium sulphate, potassium nitrate, potassium chloride, sulphuric acid, hydrochloric acid, and nitric acid between water and silica was constant. This result has been contested by van Bemmelen,[e] who points out that the distribution ratio of a substance between solid and liquid must not necessarily be constant in the case of equilibrium between solid and liquid solutions. Some solutions which originally were neutral were found to be alkaline after passing through the carbon. More recently there has appeared a very important paper by Lagergren,[f] who found that the rate at which animal charcoal absorbs succinic and oxalic acids is proportional at any time to the amount of acid which the charcoal can yet absorb. He found also that both solvent and solute could be absorbed, or, in other words, that the solution could be more concentrated or less concentrated. Thus, solutions of sodium chloride, potassium chloride, ammonium chloride, and ammonium bromide became more concentrated after contact with charcoal, while sodium nitrate, potassium nitrate, sodium sulphate, potassium sulphate, and ammonium nitrate became less concentrated. This author states that he could find no evidence of any change in alkalinity or acidity of the solutions. This behavior has

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[a] See Ostwald, Lehrbuch der Allgemeine Chemie (1891), p. 1096.

[b] Über die Adsorption gelöster Körper durch Kohle, Dissertation, Berlin (1892).

[c] Zeit. phys. Chem., **15**, 56 (1894).

[d] Jour. prakt. Chem., **23**, 324 (1881).

[e] Zeit. phys. Chem., **18**, 331 (1895).

[f] Bihang. till K. Sv. Vet.-Akad. Handl., **24**, Afd. II, No. 4 (1898).

been ascribed by the author to an increase in the density at the surface of the solid, an increase in density which involves an increase in pressure. If, therefore, an increase of pressure increases the solubility, or, in other words, if solubility is accompanied by a decrease of volume, there will be a positive absorption. But under reverse conditions there will be a negative absorption. Lagergren has calculated the degree of absorption from the surface of the solid exposed, the radius of molecular action, the density of water under different pressures. The results of the calculation for absorption of ammonium chloride and the observed absorption agree fairly well. Parallel results have been obtained where the absorbing material is kaolin and glass wool, the negative absorption of sodium chloride by kaolin having been found by van Bemmelen.[a] White china clay has been used as an absorbing medium by Cushman,[b] who finds a considerable decrease in the basic ions from solutions of ammonium chloride, barium chloride, and aluminum sulphate. The data indicate that there may have been also a negative absorption of the sulphuric acid, i. e., a considerable absorption of water from aluminum sulphate solutions, which then become more concentrated with sulphuric acid, although the author thinks the phenomena is due to the fact that owing to hydrolysis free acid necessarily exists in a solution of a salt of a trivalent base.

Many other substances have the power of absorption to a more or less degree. The solutions of such neutral salts as sodium chloride and sulphate and potassium chloride and bromide become basic when precipitated copper hydroxide is added to the solution.[c] The acid is absorbed by the copper hydroxide which then becomes green in color. The experiments of Kellner[d] show that platinum black absorbs minute quantities of acids and alkalies, but gives them up to water on standing. The experiments on absorption by silk by Walker and Appleyard[e] have shown that while picric acid is absorbed by silk from solutions in water and alcohol, yet in benzene solution there was no absorption. The nature of the solvent plays, therefore, an important rôle. The relative solubilities of picric acid in the three solvents do not throw any light on the absorptive power from the different solvents, for the solubility of picric acid in benzene lies between the solubility in water and that in alcohol. Many rock powders possess the power of absorbing the coloring matter from solutions in which the powders are suspended. The alkalinity of water in which rock powders have been in suspension has been shown in the large number

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[a] Zeit. anorg. Chem., **23**, 321 (1900).

[b] Bul. No. 92, Bureau of Chemistry, U. S. Dept. Agr., 1905, p. 18.

[c] Tommasi, Compt. rend., **92**, 453 (1881).

[d] Ann. Phys. Chem., **57**, 79 (1895).

[e] Jour. Chem. Soc., **69**, 1334 (1896).

of cases by Clarke.[a] Some powders, such as very finely powdered orthoclase, have been found to show no red color with phenolphthalein. This is due to the absorption of the color by the powder. A suspension of orthoclase in water which showed no color on the addition of phenolphthalein was allowed to settle and the supernatant solution after being poured off showed a distinct red color with a further addition of phenolphthalein. When a little of the suspended material was added to the solution again the red color disappeared from the solution, but was seen on the surface of the solid particles. The test of alkalinity of a solution by phenolphthalein can not properly be made if there is present in suspension finely divided particles which have the power of absorbing the indicator. Another substance which absorbs the phenolphthalein is magnesium ammonium phosphate.

The precipitation of a neutral calcium chloride solution by alkaline potassium phosphate solution yields a precipitate and a solution which is quite acid to litmus. The probable explanation is that the precipitated dicalcium phosphate has absorbed some of the alkaline constituents, leaving the solution acid. The abnormally acid solutions observed by Cameron and Hurst[b] when working upon iron and aluminum phosphates in solutions of various salts, were probably due to absorption effects.

Recently Hulett and Duschak[c] have investigated the nature of barium sulphate precipitates, which are nearly always found to weigh too much, and attribute the results observed by them to the formation of a compound $BaCl.HSO_4$. On long standing or heating of the precipitate hydrochloric acid was given off, facts in harmony with the assumption that hydrochloric acid was absorbed on the surface of the precipitate and escaped when the area of surface was reduced. Barium sulphate precipitates have been found to absorb many compounds from solution. Vanino and Hartl[d] observed that this precipitate absorbs colloidal metals from solution, and Patten[e] observed that salts of nickel, cobalt, chromium, iron, and manganese in solution are absorbed by barium sulphate precipitates. Korte[f] has found that not only does barium sulphate absorb salts from solution but also calcium oxalate precipitates absorb magnesium oxalate, even in the presence of ammonium chloride, and ferric hydroxide absorbs manganese hydroxide and nickel hydroxide. Ostwald[g] has called attention to similar cases.

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[a] Bul. No. 167, U. S. Geol. Survey, p. 156 (1900).
[b] Jour. Am. Chem. Soc., **26**, 885 (1904).
[c] Zeit. anorg. Chem., **40**, 196 (1904).
[d] Ber., **37**, 3620 (1904).
[e] Jour. Am. Chem. Soc., **25**, 186 (1903).
[f] Jour. Chem. Soc., **87**, 1503 (1905).
[g] Foundations of Analytical Chemistry, Trans. by McGowan, 1895, p. 26.

A solution of sodium sulphate neutral to litmus was added to a solution of barium chloride neutral to litmus in the cold. After the precipitate subsided the supernatant solution was found to be acid. The experiment was repeated, using potassium sulphate instead of sodium sulphate, and the supernatant solution was alkaline. These experiments indicate that the barium sulphate precipitate absorbs some of the constituents of the solution, that the relative amount of acid and alkali absorbed may be varied, and that the absorbing medium may act very differently toward different bases or acids.

Absorbent cotton has the power of absorbing potash from a potassium chloride solution. A tube which was filled with absorbent cotton was placed in a beaker containing a solution of potassium chloride neutral to litmus. The solution after passing up through the cotton became decidedly acid. But when potassium acetate was substituted for potassium chloride, even though a slight excess of acid was present, the solution after passing through the cotton was alkaline to litmus or phenolphthalein. Similar results were obtained by merely agitating wads of cotton in solutions of the reagents.

Finally colloidal substances have the power of absorption to a very marked degree. In numerous papers, van Bemmelen[a] has shown that all colloids absorb organic and inorganic compounds. They have the power of absorbing one of the constituents of an inorganic salt, leaving the solution acid or alkaline as the case may be. The distribution ratio of the absorbed material between water and the colloid is not constant, but depends upon the concentration of the solution.

ABSORPTION BY SOILS.

Use has been made of dyes in soil investigations by Sjollema[b] who found that different solid constituents of a soil have altogether different powers of absorption for different dyes, and this fact was made the basis of identification of some of the soil constituents. This author considers that practically all the constituents of soil, except quartz grains and undecomposed mineral fragments, are colloids, because they are colored by organic dyes. The definition of a colloid (which is thus tacitly given) seems to be much more inclusive than the generally accepted idea of colloids, so inclusive in fact as to bring such substances as carbon black, platinum black, and all other amorphous substances and also powdered crystalline substances under the head of colloids.

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[a] Landw. Vers.-Stat., **35**, 72 (1888); Jour. prakt. Chem., **23**, 324 (1881); Zeit. phys. Chem., **18**, 331 (1895); Zeit. anorg. Chem., **13**, 233 (1896); **18**, 14, 98 (1898); **23**, 111, 321 (1900); **30**, 265 (1902); **35**, 23, 338 (1904); **36**, 380 (1904); Arch. Néer. (2), **6**, 607 (1903).

[b] Jour. f. Landw., **53**, 67 (1905).

A number of experiments have been tried on several soils with dyes. When the soils were shaken up in flasks with the dye solutions or the solutions were poured through the soils, always the first runnings were clear water. With eosine solutions the eosine soon appeared in the runnings, but with solutions of methylene blue or malachite green and some other dyes, the coloring matter was held with remarkable tenacity. Separations of a mixture of eosine and methylene blue were repeatedly made in this way, the methylene blue being completely retained by the soil while the eosine was comparatively readily removed by washing. It was found that for any particular solution of a dye the various soils had a definite absorption limit; that is, if the solution is poured on a given mass of soil slowly and at a very uniform rate, there is a definite point at which the soil will cease to remove the dye and the solution will come through unchanged. Fairly good duplicate determinations for the absorptive power of any particular soil can be made in this way. The number of soils so far examined in this manner is too limited to justify generalization with any positiveness, but it would seem that the absorptive power toward a solution of methylene blue, for instance, exhibited in a number of soils was in about the same order as their known crop-producing values. Heavy soils generally absorbed more than light ones, and black, red, or dark-brown soils more than the lighter colored ones. Soils with much humus absorbed more than ones containing less of this material. Occasional apparent exceptions to these tentative generalizations have been observed. It has been found that the treatment of a soil sample with a solution of one dye does not appear in many cases, at least, to materially reduce its absorptive capacity for some other dyes; but here again observations have been too limited in number to justify generalizations. The important observation was made, however, that although an absorbed dye might be held by a soil so firmly that no appreciable amount could be washed out with water, another absorbent material might remove it with comparative readiness. Thus, a soil which had been treated with a solution of methylene blue, and was still capable of absorbing more of the material, gave no coloration to distilled water filtered through it, but did stain a filter paper and some kinds of blotting paper which were brought into contact with it.

The rate at which certain dye solutions rise in columns of dry soil has been measured and the general results are quite similar to those obtained for the rise of such solutions through paper. Two dyes first tried were safranine and methylene blue, which were absorbed but little by paper; that is, the color rose only a small distance through the paper. The same results were observed with columns of soils as with paper; namely, while the soil was moistened to a height of nearly 4 inches, the color rose only one-fourth of an inch. Three

tubes of about 0.4 inch internal diameter were filled with dry Penn loam and were packed as nearly alike as possible by tapping the end of the tube. These tubes were lowered into the liquid and the heights to which the soil was moistened were read at different times. No precaution was taken to keep the temperature constant, but temperature readings made at intervals did not vary more than 0.2° from 18° C. The following table gives the results obtained for the rise of the water from the dye solutions, and in both cases the color rose such a slight distance that it was not feasible to record any measurement on the movement of the color.

Rise of distilled water and water from dye solutions in columns of soil.

Time.	Height of distilled water.	Height wet from a safranine solution containing 2 grams per liter.	Height wet from a methylene blue solution containing 2 grams per liter.	Time.	Height of distilled water.	Height wet from a safranine solution containing 2 grams per liter.	Height wet from a methylene blue solution containing 2 grams per liter.
Minutes.	*Inches.*	*Inches.*	*Inches.*	*Minutes.*	*Inches.*	*Inches.*	*Inches.*
1	0.30	0.35	0.35	30	1.95	1.82	2.15
2	.45	.50	.60	40	2.32	2.15	2.49
3	.62	.65	.73	50	2.57	2.35	2.72
4	.73	.75	.83	60	2.80	2.60	2.96
5	.80	.83	.88	75	3.08	2.87	3.25
7	1.00	.95	1.05	90	3.35	3.13	3.52
10	1.15	1.10	1.25	105	3.62	3.45	3.77
15	1.42	1.33	1.55	120	.....	3.65	3.90
20	1.62	1.53	1.83				

It will be observed that the rate at which distilled water rose was intermediate between the rates at which the soils became moist from the two dye solutions. These differences are, however, not great enough to warrant any general conclusions, because they might be attributed to slight differences in the packing of the soil in the tubes. It is interesting to note that the same formula, $y^n = kt$, which was found to describe the facts in the case of the movement of water and dye solution through paper, also describes the facts remarkably well in this case

Two other dyes were tried, coralline and indigo carmine, which move through paper rather readily. It was found very difficult to read the height to which the dye had risen, because it would rise to a considerable height on one side of the tube and would scarcely rise at all on the other side, in some cases the difference being as great as 1 inch. However, a rough estimate was made of the average height of the dye in the tube when viewed from all directions. It was not found difficult to measure the height to which the water rose, for in no case were differences of level more than one-quarter of an inch. The following results were obtained for the same kind of soil as before, Penn loam, and at the same time the rate at which coralline rose in Podunk fine sandy loam was measured. The temperature was 21.5° C.

Rise of distilled water and dye solutions in columns of soil.

Time.	Penn loam, height of distilled water.	Penn loam, indigo carmine, 2 grams per liter.		Penn loam, coralline, 2 grams per liter.		Podunk fine sandy loam, coralline, 2 grams per liter.	
		Height moistened.	Height colored.	Height moistened.	Height colored.	Height moistened.	Height. colored.
Minutes.	*Inches.*	*Inches.*	*Inches.*	*Inches.*	*Inches.*	*Inches.*	*Inches.*
0.5	.....	.....	.....	.....	.....	1.35	.....
1	0.45	0.50	0.25	0.40	.....	1.95	.....
1.5	.....	.....	.....	.....	.....	2.50	.....
2	.60	.65	.35	.53	.....	2.90	0.60
3	.72	.80	.....	.63	.....	3.50	.....
4	.81	.88	.....	.75	.....	4.10	.....
5	.89	.97	.40	.82	.....	4.55	.90
7	1.01	1.10	.....	.93	.....	5.30	.....
10	1.16	1.25	.....	1.10	.....	6.20	1.00
15	1.35	1.45	.....	1.36	.....	7.40	1.10
20	1.52	1.67	.75	1.58	.....	8.25	.....
25	.....	.....	.....	.....	.....	8.95	1.20
30	1.82	1.99	.....	1.82	0.20	.....	.....
40	2.10	2.25	1.05	2.13	.27	.....	.....
50	2.30	2.50	1.25	2.36	.....	.....	.....
60	2.52	2.69	.....	2.58	.30	.....	.....
75	2.81	2.91	.....	2.77	.....	.....	.....
90	3.13	3.25	1.40	3.12	.35	.....	.....
105	3.40	3.50	.....	3.30	.....	.....	.....

The above table indicates that for Penn loam the rate at which the soil becomes moist is the same for the dye solutions as for distilled water. The results can be described very well by the general equation $y^n = kt$. The table also shows the widely different results when two different types of soil, a loam and a sandy loam, are employed, the rate on the latter being over five times that in the loam soil.

In general, papers seem to be better absorbers of dyes than are soils. But, on the other hand, some substances, such as alkalies, are generally absorbed more powerfully by soils than by papers. This has an important bearing on the common practice of testing the reaction of a soil with moist litmus paper. Blue litmus, as is well known, is the sodium salt of the red dye. In aqueous solution it must be considerably hydrolized, so that when a paper saturated with it is brought into intimate contact with a soil the base is absorbed more readily by the soil and the remaining acid more readily by the paper, with the consequence that the latter becomes red. This explanation of the reddening of litmus paper by soils was confirmed by other experiments. Strips of sensitive blue litmus paper were wrapped in absorbent cotton moistened with distilled water freed from carbon dioxide and showing no reaction with a very sensitive specimen of litmus. A slight pressure was applied in order to insure intimate contact. In the course of about fifteen minutes the litmus paper had become decidedly pink, apparently showing an acid reaction. Two wads of this same cotton were placed in beakers, one containing a solution of potassium chloride neutral to litmus and the other containing potassium acetate with a slight but sufficient excess of acetic acid to redden litmus. Within a few minutes the supernatant liquor in the beaker containing potassium chloride had

become distinctly acid, as shown by the further addition of litmus, while the supernatant solution in the beaker containing the acetate had become distinctly akaline to both litmus and phenolphthalein. It is obvious, therefore, that the reddening of the litmus was a true absorption effect. It might be argued from these experiments that the only test as to the presence of an acid in a soil is the formation of an acid solution when extracted with water. It is true that this is the only satisfactory criterion which suggests itself. But as the experiments just cited show, soils and other absorbent substances can and do absorb acids, some more than others, and it is quite possible that an absorbed acid, which was not easily removed from a soil by water, might be removed by paper, if paper were the better absorber for that particular acid. It is well, therefore, to view with caution the prevalent notions as to the wide distribution of acid soils founded on a very uncertain criterion, and especially in view of the fact that the great majority of soils yield aqueous extracts which on heating in platinum show alkaline reactions. Most of our field crops can withstand a fairly high concentration of acid, but clover[a] is especially sensitive, being inhibited in growth by concentrations less than twenty thousandth normal (N/20,000). Yet we have observed several cases and others have been called to our attention where clover was found growing well in soils apparently very acid, the true explanation being undoubtedly that the supposed estimation of acidity was in fact a measurement of the absorptive capacity of the soil.

Furthermore, it is probably fallacious to assume that the acidity of a soil can be estimated by adding calcium hydrate, ammonia, or other alkalies in solution until the soil will turn red litmus paper blue when the paper is brought into contact with the soil, since it has been clearly shown that most soils absorb these substances much more effectively than does litmus paper. If these solutions be added to the soil slowly (for absorption is not an instantaneous process, but requires appreciable time to attain equilibrium) it is frequently astonishing how much alkali can be taken up before an alkaline reaction can be detected by the test paper, a fact repeatedly observed by various investigators, but the significance of which has not hitherto been recognized.

From the foregoing paragraphs evidence has been adduced which establishes the following facts:

That soils are unusually good absorbents.

That they absorb many and various kinds of organic materials, showing marked selective powers.

That the absorption of one organic substance does not generally interfere with the absorption of another, but may even augment it.

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[a] Cameron and Breazeale, Jour. Phys. Chem., 8, 1 (1904).

That inorganic substances are markedly åbsorbed, selective absorption from mixtures being pronounced even among the dissociation products of electrolytes.

That the absorption of organic substances is markedly influenced by the presence of inorganic substances, and vice versa.

That it is significant that those substances which are prominent as fertilizer constituents, namely, calcium, potassium, phosphoric acid, ammonia, and proteid organic matter, are substances which are markedly absorbed by soils; and, finally,

That the reactions which might ordinarily be expected to take place among these substances may be and probably are very much modified when they take place in the presence of the absorbing surfaces.

CHEMICAL REACTIONS AT SURFACES.

That surface influences are very potent in chemical reactions has long been known, and within the last few years has been receiving general recognition. It seems desirable, however, to emphasize this point by a few brief references. Cayhuse and Thenard[a] early noted the influence of the walls of the containing vessel on the decomposition of hypochlorous acid. Langer and Meyer[b] showed that carbon dioxide dissociates more readily and at a much lower temperature in a porcelain vessel than in a platinum one, and Meyer and Freyer[c] showed that oxygen and hydrogen in a silver-coated vessel will unite at a temperature more than 250° C. lower than in an ordinary glass vessel. Kooij[d] found that phosphine decomposed nearly three times as rapidly in an old vessel as when in a new one, and Cohen[e] found that the decomposition of arsine is greater in a new vessel than in one which has become coated with arsenic.

Bone and Wheeler,[f] Meyer and Krause,[g] Meyer and Askenasy,[h] Gautier and Hélier[i] found the nature of the walls of the containing vessels to have a marked influence on the union of hydrogen and oxygen. Berthelot[j] showed that this reaction was much affected by barium hydrate, alkalies, manganese, etc., which are probably present on the surfaces of various glasses. Van't Hoff[k] has shown the influence of the walls of the vessel and various treatments of them upon a number of reactions, and concludes that the influence is dependent upon both the nature and amount of the surface exposed.

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[a] Compt. rend., **40**, 935 (1855).
[b] Pyrochemische Untersuchungen, 1885, p. 64.
[c] Ber., **25**, 622 (1892).
[d] Zeit. phys. Chem., **12**, 155 (1893).
[e] Ibid., **20**, 303 (1896).
[f] Jour. Chem. Soc., **81**, 538 (1902).
[g] Ann. Phys. Chem., **264**, 85 (1891).
[h] Ibid., **269**, 49 (1892).
[i] Compt. rend., **122**, 566 (1896).
[j] Ibid., **125**, 271 (1897).
[k] Études, 1884, p. 55.

Raymond and Sulc[a] and Plyak and Husek[b] have found that inversion of cane sugar is affected by the nature of the walls of the vessel. Urech[c] has shown that the reduction of Fehling's solution is dependent upon the amount of surface exposed by the containing vessel and the amount of cuprous oxide formed during the reaction. Liebreich[d] cites an experiment of Monckman in which no chloroform was formed by the action of alkalies on chloral when brought together in capillary tubes, although the reaction takes place readily under ordinary conditions. Liebreich, Becquerel,[e] Lieving,[f] Lloyd,[g] Dale,[h] Spring,[i] Bredig and von Berneck,[j] Thomson,[k] and others have given numerous examples of the modification or even complete change in the character of known reactions when carried on in capillary tubes.

The effect of the size of solid particles has been shown by Ostwald[l] to have an influence on the solubility. Thus he found that the solubility of very finely divided mercuric oxide is greater than that of coarse mercuric oxide, and Hulett[m] has demonstrated that finely divided gypsum has a solubility of 20 per cent more than massive gypsum. This difference in solubility has been attributed to the difference between the surface tension on a plane and on a curved surface.

From this work have come some of the most interesting developments of modern theoretical chemistry, which can not be discussed here. The citations given do, however, emphasize in the most positive way the enormous importance of surface effects in modifying or bringing about chemical reactions, and it is perfectly obvious that unless such effects or the possibility of their existence are fully realized no material progress can be expected in the study of the chemistry of the soil.

FLOCCULATION.

Closely allied to the phenomenon of absorption, and in a certain way parallel to it, is the phenomenon of flocculation by solutions. Colloids and also crystalline substances in a very fine state of division are caused to settle more readily from suspension in a liquid in the

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[a] Zeit. phys. Chem., **21**, 481 (1896); **33**, 47 (1900).

[b] Ibid., **47**, 733 (1904).

[c] Ber., **15**, 2687 (1882).

[d] Berliner Sitzungsber., 1886, p. 959; Zeit. phys. Chem., **1**, 194 (1887); **5**, 929 (1890); Phil. Mag. (5), **23**, 468 (1887); **29**, 216 (1890).

[e] Compt. rend., **65**, 51, 720 (1867).

[f] Proc. Cambridge Phil. Soc., **14**, 370 (1883–1889).

[g] Chem. News, **51**, 51 (1885).

[h] Manchester Memoirs (3), **10**, 1 (1885).

[i] Bul. Acad. Roy. Belg. (3), **30**, 37 (1895); Zeit. anorg. Chem., **8**, 424 (1895).

[j] Zeit. phys. Chem., **31**, 258 (1899).

[k] Applications of Dynamics to Physics and Chemistry, 1888.

[l] Zeit. phys. Chem., **34**, 496 (1900).

[m] Ibid., **37**, 385 (1901).

presence of certain electrolytes, while other electrolytes cause a breaking up of the flocculation and may absolutely hinder the subsidence of these suspended particles. While there are certain generalizations concerning the flocculation of the finer particles of a soil suspension, the question of the flocculation of colloidal solutions and suspensions has received more detailed investigation. This is probably to be attributed to the fact that the actual composition of the finer particles of a soil varies, while with colloidal solutions and suspensions we have a certain definite knowledge of the chemical composition of the solution, even if the chemical nature is not very well understood.

It has been proved by Barus[a] and Bodländer[b] and later confirmed by Freundlich[c] that the power to flocculate colloids is possessed exclusively by electrolytes. Of the large number of nonelectrolytes which have been tried, not one has been found which possesses in any degree the power to precipitate a colloid from solution or suspension. The flocculating power of any salt depends on one of the ions in the case of any specific colloid.

The flocculation of colloids by electrolytes has been investigated by Schulze,[d] Hardy,[e] and many others, who find that the flocculating powers of different cations depend greatly on the valence. Schulze found the flocculating power of the salts of univalent, bivalent, and trivalent metals to be in the proportion of about 1:30:1650. This has been ascribed by Bredig[f] and Spring[g] to the hydrolysis of the salt, the degree of which increases very rapidly as the valence of the cation increases. Moreover, Linder and Picton,[h] and also Whitney and Ober[i] have observed that the flocculated colloid absorbs small quantities of the metal hydroxide, leaving the solution, which was originally neutral, weakly acid. Freundlich,[j] however, has found that the flocculating power of barium salts, which are scarcely hydrolized, is almost equivalent to that of glucinum salts and of uranyl nitrate, both of which are strongly hydrolized. As both of these salts have a bivalent cation it follows that the degree of hydrolysis exerts no influence. This author comes to the conclusion that the precipitating power of an ion is dependent upon its valence, upon the migration velocity of the ion (in the case of univalent ions), and upon the specific nature of the electrolyte. The precipitation of egg albumin

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[a] Am. Jour. Sci., **37**, 122 (1889).
[b] Nach. K. Ges. Wiss., Göttingen, 1893, p. 267.
[c] Zeit. phys. Chem., **44**, 136 (1903).
[d] Jour. prakt. Chem., **25**, 431 (1882); **27**, 320 (1883).
[e] Proc. Roy. Soc., **66**, 111 (1900); Zeit. phys. Chem., **33**, 385 (1901).
[f] Anorganische Fermente, 1901, p. 15.
[g] Bul. Acad. Roy. Belg., 1900, p. 483.
[h] Jour. Chem. Soc., **67**, 63 (1895).
[i] Jour. Am. Chem. Soc., **23**, 842 (1901); Zeit. phys. Chem., **33**, 385 (1901).
[j] Zeit. phys. Chem., **44**, 129 (1903).

by ammonium sulphate solution has been recently shown by Galcoth[a] to be a completely reversible process, for in saturated solution of the salt all the albumin was precipitated, and after dilution with water none of the albumin went back into solution. Colloidal suspensions have been divided into two classes, those which migrate toward the cathode under electrical stress and those which migrate toward the anode. The colloids which migrate toward the cathode are precipitated by anions, and vice versa. This migration of the colloids resembles the behavior of an electrolyte, and the theory has been advanced that colloids in solution are in reality large aggregations with small electrical charges,[b] which are counterbalanced by the presence of ions carrying the opposite charge. There is apparently an equilibrium between the two, and a disturbance of the equilibrium by the addition of a salt to the solution tends to precipitate the colloid, which always carries down with it ions of the opposite charge. Further, both classes of colloidal suspension have the peculiarity that any one is precipitated from the solution when added to a suspension of one of the other class, the precipitate being of course a mixture of the two. Thus Linder and Picton[c] found that a solution of aniline blue (anode convection) would precipitate a solution of magdala red (cathode convection), and Freundlich[d] found that a colloidal solution of arsenic sulphide (anode convection) would precipitate a colloidal solution of ferric hydroxide (cathode convection). The addition of a solution of an electrolyte to the mutually precipitated colloids has been shown by des Bancels[e] to change the character of the precipitate. Under these circumstances the colloid, which is normally precipitated by the electrolyte alone, persists. Moreover, it was also found that with a small or a large concentration of the electrolyte, both colloids were precipitated. In the former case there is undoubtedly incomplete precipitation of one colloid by the electrolyte, the residue causing a mutual precipitation of both colloids, while in the latter case the great concentration of both positive and negative ions of the salt precipitates both colloids. Bredig[f] has found that the addition of gelatine in colloidal *solution* increases very much the stability of a colloidal *suspension* of a metal. Mathews[g] suggests that the precipitation of colloids by electrolytes is brought about by an alteration of the surface energy of the colloid, and the precipitating power of the

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[a] Zeit. phys. chem., **44**, 461 (1905).

[b] Duclaux [Compt. rend., **140**, 1544 (1905)] regards the granules of a colloidal solution to be of such magnitude that they may be regarded as conductors of electricity.

[c] Jour. Chem. Soc., **67**, 63 (1895).

[d] Zeit. phys. Chem., **44**, 129 (1903).

[e] Compt. rend., **140**, 1647 (1905).

[f] Anorganische Fermente, 1901.

[g] Amer. Jour. Phys., **14**, 203 (1905).

electrolyte is determined primarily by the solution tensions of the ions. The ion of the opposite sign of the colloid precipitates. The ion of the same sign is not inert, but, in the case of collodal egg albumin, tends to dissolve the colloid. He also concludes that the product of the concentration of the precipitating ion by the "tension coefficient" is a constant, a relation which was found to hold approximately in experiments with egg albumin.

The precipitation of finely divided solids in suspension resembles in a remarkable way the precipitation of colloids. It has been frequently observed in the laboratory that the suspended material causing the cloudiness of the Potomac water as it comes from the faucets will settle if an acid or a strong salt be added to the water, but the addition of a base, and especially ammonia, will prevent the flocculation and subsidence for several months. The same is true of almost every suspension of finely divided particles of soil.

The flocculation of precipitates is generally brought about by the addition of electrolytes. It has been observed by De Lucca and Ubaldini[a] and by Sobrero and Selmi[b] that the precipitate of sulphur formed when aqueous solutions of hydrogen sulphide and sulphur dioxide are mixed will settle quickly in the presence of salts of the alkalies and alkaline earths. Stengl and Morawsky[c] have confirmed this result, and have found that potassium and barium salts precipitate sulphur in a plastic condition, while the salts of sodium, calcium, and magnesium precipitate it in a flocculent condition. Ebell[d] has shown that finely divided particles of ultramarine were flocculated by small quantities of sodium hydroxide, sulphate, nitrite, etc. Suspensions of kaolin in water have been precipitated by Bodländer[e] by minute quantities of an electrolyte, while considerable quantities of nonelectrolytes produce no flocculation whatever. Thoulet[f] advanced the theory that at the surface of the solid there was adsorbed a more concentrated solution of the electrolyte, which increased the density of the particle so much as to cause precipitation. Barus and Schneider[g] have shown that the rate of flocculation depends on the temperature, the dilution, and the quantity of foreign material present in solution.

The observations regarding flocculations in soils recorded by various agricultural investigators are conflicting and very confusing. It is generally held that acids induce flocculation, but it has been observed that some acid soils, while wetting with extreme difficulty, when once wet puddle badly and hold the water with unusual tenacity. On the other hand, alkalies are generally held to inhibit or break up floccu-

[a] Compt. rend., **64**, 1202 (1867).
[b] Ann. Chim. Phys. (3), **28**, 210 (1850).
[c] Jour. prakt. Chem. (2), **20**, 76 (1879).
[d] Ber., **16**, 2429 (1883).
[e] Jahrb. f. Min., 1893, II, p. 147.
[f] Compt. rend., **91**, 1072 (1884).
[g] Zeit. phys. Chem., **8**, 278 (1891).

lation and induce puddling, as is so often observed in soils containing "black alkali" or sodium carbonate in noticeable amounts. Ammonia is very efficient in breaking up flocculation. But lime is just as efficient in inducing and promoting flocculation,[a] though some authorities maintain that an excessive amount of lime does break up flocculation and cause puddling. Hilgard[b] found the flocculation of soil particles to be inversely proportional to their size. Increase of temperature decreased flocculation. Alcohol and ether decreased flocculation, as did also alkalies, while neutral salts and acids induced flocculation, as did also lime. The greater the density of the particle the less the tendency toward flocculation. This author also called attention to the effect of the "alkali" in the arid regions which sometimes renders the soil absolutely impermeable. Whitney has also given considerable attention to flocculation[c] in his early publications, considering especially its effect on the adaptation of special crops to soils.

It is probable from the few references to the available literature which have been here cited that the presence of mineral salts arising from the disintegration of the minerals of the soil play an important rôle in the texture of the soil. The extremely great dilution of an electrolyte, which causes precipitaiton of finely divided matter, whether it be in the colloidal state or not, is of the same order of magnitude as the soil solution. It is therefore extremely probable that the presence of those dilute solutions in the soil keeps the passages between the soil grains open. This phenomenon is undoubtedly of importance also in reducing the amount of surface exposed to the solvent action of the soil water, and probably modifies to some extent the absorbent power of the soil.

GENERAL DISCUSSION AND SUMMARY.

In the foregoing pages it has been shown that as a rule—

(1) *The soil contains all the common rock-forming minerals.* There may be, indeed probably are, extreme cases for which this statement would not be strictly accurate, but it may be regarded as a rule holding quite rigidly for practically all arable soils. It has further been shown that the weight of available evidence justifies the further generalization that—

(2) *Some, at least, of each mineral species in the soil is presenting surfaces of the mineral as such to the solvent action of the soil water.* This being the case it follows that—

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[a] See Whitney, Bul. No. 5, Division of Agricultural Soils, U. S. Dept. Agr., 1896, p. 9.

[b] Forsch. Geb. Agr. Phys., 2, 441 (1879).

[c] Fourth Annual Report, Maryland Expt. Stat. (1891), p. 258; Bul. No. 4, Weather Bureau, U.S. Dept. Agr. (1892), p. 80. See also Wiley, Principles and Practice of Agricultural Analysis I, 1894, p. 171.

(3) *The minerals of the soil will continue to dissolve.* On dissolving the minerals carrying the stronger basic or acidic constituents will be more or less completely hydrolized, and generally the stronger hydrolization product will remain in solution and the weaker one will be more or less completely precipitated. It is thus that the principal mineral plant-food constituents are brought into solution and made available to the plant.

What concentration the soil moisture actually possesses has been determined with what may be regarded as approximate accuracy. Two methods have been devised[a] for extracting the free solution actually existing in a soil, and analyses of a number of such extracts obtained from several types of soil of widely different origin and composition have yielded an average for potassium (K) of 27.3 parts and for phosphoric acid (PO_4) 8.5 parts per million of solution. The approximate uniformity of the individual results makes it appear improbable that further accumulation of data would change these average figures materially. We have as yet no reliable data as to the actual concentrations of the mineral plant-food constituents requisite for plant growth, and very meager data even for the most desirable or optimum concentrations[b]. Birner and Lucanus[c] many years ago found that mature crops of good yield could be grown in a well water containing about 18 parts potassium (K) and about 2 parts phosphoric acid (PO_4) per million of solution; and very satisfactory growth of wheat has been obtained in the water from the Potomac River, which contained about 7 parts per million of potassium. It appears, then, that soils do in general yield enough mineral constituents to the soil waters to furnish the nutrient material needed for plant growth, a conclusion advanced by Johnson[d] and supported by many subsequent investigators. The conclusion has not gone unchallenged, however, as in a recent publication of Snyder,[e] who tried unsuccessfully to grow grain crops in sand watered with soil leachings, ignoring the relatively enormous absorptive power of the soil in the pots containing his cultures. Moreover, in such experiments the fact is ignored that on account of these absorptive powers of a soil the leachings from it are always of a decidedly less concentration than the solution in the soil from which plants growing on that soil would feed. It seems fair to assume that the negative results occasionally obtained with sand cultures are more than outweighed by the positive and more

[a] Bul. No. 22, Bureau of Soils, U. S. Dept. Agr. (1903), p. 16; Briggs and McCall, Science, **20**, 566 (1904).

[b] Breazeale, Science, **22**, 146 (1905).

[c] Landw. Vers.-Stat., **8**, 128 (1866).

[d] How Crops Feed, 1884, p. 322.

[e] Bul. No. 89, Minnesota Exp. Stat., 1905.

easily controlled, and therefore more certain results of numerous water cultures.

It has been found in some cases when wheat seedlings have been grown for weeks in a small amount of soil confined in a paraffin basket[a] that there is a diminution of the amount of potassium and possibly also of phosphoric acid, which will be removed by a three-minutes extraction with water. This would indicate that in such cases where there is but a small amount of soil there is a removal of these constituents from the soil solutions by plants more rapidly than the minerals restore them to the solution. The solubility of the minerals involves a considerable time element in order to approximate equilibrium conditions, and the magnitude of the figures obtained with a given amount of minerals or soil and water is smaller than that which available data show from the water in practically all soils, and further show to be maintained throughout a growing season. Under field conditions, however, and in artificial cultures with larger amounts of soil, another factor must be considered.

It has been pointed out on a preceding page that there is a movement of the water which a soil contains, probably slow, but steady, toward the surface of the soil. This movement results as a consesequence of the evaporation at or near the surface of the soil, and is a capillary phenomenon, the soil solution passing through the capillary spaces among the interstices of the soil or in films over the soil grains. In this slow upward movement over the soil grains the soil water can and undoubtedly does take into solution the products of solution and hydrolysis, becoming more and more concentrated. On evaporation at the surface or in the upper soil layers the dissolved material is there concentrated as a result of this process, which King has designated "capillary sweeping." In this way the concentration of the soil solution in the root zone is not only being maintained by solution of the minerals with which it is then in contact, but by the transportation of solution products from lower depths, the extent of which in some cases is unquestionably great. On the other hand, the percolation and drainage of water downward through a soil, as after a rain or irrigation, is a gravitational phenomenon and takes place to a very limited extent, if at all, through the capillary interstices, but almost entirely through the larger openings. As compared with the "capillary " movement upward, this "gravitational" movement downward is quite rapid. As a result, but comparatively little of the material already in solution in the soil goes into the "gravitational" water, and when this downward movement ceases and evaporation at the surface again proceeds, the dissolved material continues to move upward with but probably slight diminution in quantity.

[a] Bul. No. 23, Bureau of Soils, U. S. Dept. Agr., 1904.

This explanation of the movement of ground waters is, with slight modifications, due to Means[a]. It further explains why drainage waters and the waters of wells, springs, etc., generally have a lower concentration than the soil solution normally possesses. It has, furthermore, been repeatedly substantiated by laboratory experiments with soil columns of various heights, and these experiments can readily be made a laboratory procedure for students' instruction as well as offering a valuable method of research.

Since practically all soils contain the same minerals and essentially the same processes are taking place in all of them it would follow that about the same solution should be expected in all soils, except in so far as changes were introduced by differences in absorptive powers of the solids, rates of movement of water, etc. Examinations of a large number of soils, many of which have been already published, established empirically that these considerations are justified. It has been found that the concentrations of the mineral constituents in soil solutions vary, as would be expected from the above considerations, the percentage variation being sometimes large, though considered from the point of view of the absolute amounts involved the variations are actually quite small. This generalization may be formulated then:

(4) *The concentration of the soil solution, with respect to the principal mineral plant food nutrients, is sufficient for the growth and development of crops. And, further, the magnitude of the concentrations is the same for practically all soils.*

The effect of surfaces in modifying not only in intensity, but even in kind, the reactions taking place in solutions in contact with them has been emphasized in foregoing paragraphs. The importance of such effects is now being realized by many investigators, as the citations will show, and in a recent publication[b] from this Bureau the conclusion was drawn that "on the average farm the great controlling factor in the yield of crops is not the amount of plant food in the soil, but is a physical factor, the exact nature of which is yet to be determined." But though the exact nature of these several effects is not yet clearly understood, much information about them is rapidly accumulating, and their obvious importance in soil investigations should not be the least of the factors making for the development of this field of inquiry. Not only the physics of the soil, but even more vitally is soil chemistry involved, and it can not be too strongly insisted that the chemistry of the soil is not the ordinary chemistry of the beaker. Intimately associated with this subject is the nature of the organic matter of the soil, not only as the solid

[a] Science, **15**, 33 (1902).

[b] Bul. No. 22, Bureau of Soils, U. S. Dept. Agr., 1903, p. 63.